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Centre for Energy Research

Progress Report  
on Research Activities

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PROGRESS REPORT  
ON RESEARCH ACTIVITIES  
IN 2014

Dear Reader!

Welcome to the yearbook published by the MTA Centre for Energy Research, summarizing its recent scientific results and highlights. This booklet also provides a brief introduction of the departments and research groups working in the Centre.

In the year 2014, our Institute for Atomic Energy Research started the preparations for an independent review of the safety analysis of the new nuclear reactors to be installed at Paks site. Within the frame of the Hungarian Sustainable Nuclear Technology Platform we submitted a proposal to the Hungarian Government, which was evaluated and highly ranked. The research topics in the proposal, formulated by five member institutions of the Platform, were arranged in three main chapters: *i)* multiphysics modelling of phenomena in nuclear reactors, *ii)* experimental research, *iii)* management of spent fuel and radioactive waste, research of Generation IV reactors.

The first European research calls in Horizon2020 have been published in 2014. Within the Euratom program, the safety of nuclear reactors is emphasized. After a long stand-by period, the Centre will again participate in European research programs, where the severe accident facility, CODEX, and the PMK water loop facilities will be used in international experimental research projects. In addition to the European collaboration, the Joint Korean-Hungarian Laboratory will continue its research program with similar aims.

The space dosimetry team has achieved a major step with the accomplishment of rocket experiment campaign. The new active radiation instruments were used to detect radiation up to 100km from the Earth's surface.

With its strategy revised two years ago, the Research Centre is committed to actively participate in the discussions on energy supply, security and environmental safety. Renewable energy sources have gained increased interest in the recent year. However, integration of intermittent renewable energy production in the energy system must be supported by the use of energy storage.

Since the construction of a pumped hydro plant in Hungary does not seem likely in the near future, other technologies were also investigated. Our results have shown that the joint concept of the application of dynamic pricing and the use of energy storage is able to support the integration of intermittent renewable sources, without increasing the total amount of subsidies.

A new research field, water oxidation catalysis, is under investigation with the short-term objective to explore adaptable ways to efficient catalysis. The long term objective is to find catalysts that can make part of a complex (photo) catalytic water splitting system. Hydrogen, as the fuel of future energy production devices, has the potential to decrease our dependence on fossil sources, but challenges in the cost effective production, storage and safety have to be coped with by assiduous research.

Ákos Horváth  
Director General

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## **I. RESEARCH RELATED TO NPPS**

# MULTI-PHYSICS APPROACH OF THE SAFETY ANALYSIS HOT CHANNEL CALCULATIONS; SPECIFICATIONS AND DEVELOPMENT OF THE COMPUTATION ENVIRONMENT

*Ádám Tóta, István Panka, András Keresztúri, János Gadó*

## Objective

The hot channel calculation is the important final phase of the safety analysis because the fulfillment of the acceptance criteria is investigated here. In fact, it would require simultaneous application of several disciplines like reactor physics, thermo- hydraulics, material science and mechanics. Nevertheless, the traditional approach to this problem is that the applied calculations are focusing on only one or two disciplines while the influence of the other ones are taken into account in an approximate manner which can result in an insufficient coupling between the different disciplines. Establishing an online coupling between the neutron physics, the fuel behavior and the thermo-hydraulic codes would be unavoidable for the best estimate parallel handling of the processes important for the safety analyses.

## Methods

The remedy of the problem outlined above can be based only on parallel, tightly coupled and detailed models of all disciplines, which is called "multi-physics". The constituent models are depending on the specific problem to be solved. In the present work, we focus on the hot channel calculations of various transient events. In the frame of the project, the most important phenomena – to be modeled in parallel – are the thermo- hydraulics of the coolant, especially the mixing, the corresponding surface heat transfer process and the heat conduction inside the fuel pin, especially in the gap, moreover the feedback effects of the reactor physics. In 2014, the detailed specification of the computer code coupling and the development of the computational environment to be applied for their parallel running were foreseen.

## Results

The modeling tools intended to be used are the followings: ATHLET for the thermo-hydraulic system, COBRA for the hot-channel thermo-hydraulics and mixing, FUROM and FRAPTRAN for the stationary and the transient fuel behavior, KARATE for the stationary neutron physics and the KIKO3DMG for the neutron transient calculations. The variables of the mentioned codes were classified according to standpoints of the data exchange and the supposed iteration between them [1]. The control points and the further necessary modifications in each module were determined. Moreover, the relationship between the stationary and the transient calculations were clarified on the level of the module variables. The software framework to be filled with the appropriate modules is capable for both the stationary and the transient multi-physics calculations. The computation environment was specified in two alternative ways [1].

In case of the first solution, the INTEL FORTRAN service function "USE DFWIN" was applied for sharing selected memory parts between separately parallel running processes, which gave the possibility to develop our own FORTRAN subroutines for assuring synchronization, too. This solution is ready to use. The alternative, second type software framework is based on the use of the MPI (Message Passage Interface) library to communicate between the parallel running modeling tools.

In case of open assemblies it turned out that the appropriate modeling of the coolant mixing effects can require a full core thermo-hydraulic analysis [2]. A coupled two level – course and fine mesh – modeling had to be developed for this purpose in order to achieve realistic computational time [3]. The coupling methodology between the two levels was investigated and effective spacer drag coefficients were defined for the bundles.

## Remaining work

The second type software framework based on the MPI library is being developed.

## Related publications

- [1] Á Tóta, I. Panka, A. Keresztúri, J. Gadó, "Specification and software design of the multi-physics calculations", MTA-EK-RAL-2014-951/1-M0 report in Hungarian, (2014)
- [2] Á. Tóta, A. Keresztúri, I. Panka, A. Molnár, E. Temesvári, "Investigation of the hot-channel calculation methodology in case of shroud-less assemblies", *Kerntechnik*, 79/4 (2014), pp. 351-358
- [3] Á Tóta, I. Panka, A. Keresztúri, "Hot channel and assembly level thermal hydraulic calculations", MTA-EK-RAL-2014-282/2-M0 report in Hungarian, (2014)



# INVESTIGATION OF TEMPERATURE FLUCTUATIONS CIRCULATING IN THE PRIMARY COOLANT OF A VVER-440 REACTOR

Sándor Kiss, Sándor Lipcsei

## Objective

Reactor noise diagnostics is based on statistical investigation of the fluctuations of various reactor parameters in steady state of the reactor. In PWRs small reactivity fluctuations are partly induced by temperature fluctuations of the coolant passing through the reactor core. The main source of these temperature fluctuations travelling with the coolant is the reactor itself. Perturbations arisen in the core and circulating in the primary loop return into the reactor after being attenuated in the steam generators. This kind of feedback depends on circulation period, phase and time history of the perturbations. Time history of a perturbation is mainly determined by the transfer properties of the steam generator. Measured circulation period of the perturbations may differ significantly from the result of the calculation based on the total mass and mass flow rate of the coolant. According to our investigation, this difference can mainly be attributed to the structure of the steam generator.

## Methods

In order to analyze the transfer properties of the steam generators, first the transit time of the coolant and of the perturbations was calculated, taking into consideration the structure of the steam generators (more than 5000 heat exchanger tubes of different lengths between 8 and 14 m, two collectors). Then frequency response and attenuation of the steam generator were determined using this transit time and the thermal-hydraulic properties of the steam generator.

## Results

The main task of the steam generator is to extract the energy released in the reactor core by cooling the primary coolant. As a consequence of the cooling, temperature fluctuations travelling with the coolant are significantly damped, as well.

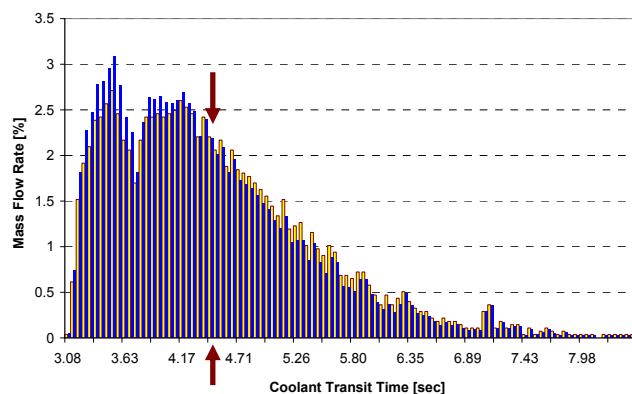


Fig. 1: Distribution of the mass flow rates as a function of the transit time with (blue) and without (yellow) correction for different heat exchanges in the different lengths of tubes (average transit time is marked with red arrows)

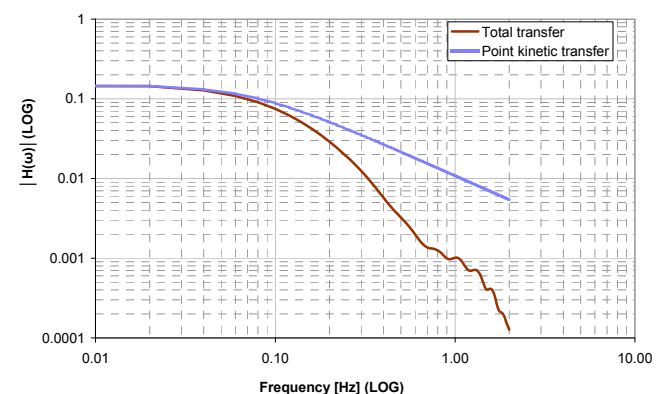


Fig. 2: Transfer function of the steam generator. It can be seen, the effect of the steam generator's structure on the transfer properties (red) comparing to pure dynamical behaviour (blue)

Some parts of the coolant pass through the steam generator quicker, while other parts pass slower, because of the different lengths of the heat exchanger tubes used. This phenomenon has several consequences. Due to the mixing after passing through the different lengths of tubes over different time intervals and due to the different heat exchange, perturbations broaden in time, and the maximum of their distribution is located at a transit time smaller than the average transit time (see Fig. 1). Effectively the steam generator filters out the frequency components of the temperature fluctuations above 1 Hz (see Fig. 2). New perturbations developed both in the reactor vessel and in the steam generator, the ratio of them was estimated [2]. However, more investigations are needed to analyze the development mechanism inside the reactor.

## Remaining work

Investigation would be continued with analyzing the way of propagation and development of temperature fluctuations inside the reactor vessel.

## References

- [1] S. Kiss, S. Lipcsei: *Effect of the steam generator on temperature fluctuations of the primary circuit coolant in VVER-440 reactors*, Ann. Nucl. Energy **72**, 166 (2014)
- [2] S. Kiss, S. Lipcsei: *Investigation of Coolant Temperature Fluctuations Circulating in the Primary Circuit of VVER-440 Reactors*, The 23rd International Conference Nuclear Energy for New Europe, 2014. September 8-11, Portorož, Slovenia

## List of abbreviations

PWRs      Pressurized Water Reactors

# CONSERVATIVE ESTIMATION OF FUEL FAILURE IN LARGE BREAK LOCA ACCIDENTS

*Péter Szabó, Zoltán Hózer, Emese Slonszki*

## Objective

The international practice of the determination of in-containment source term for large break LOCA accidents was reviewed in order to support reduction of currently used 100% failure rate to more realistic, but still conservative value.

## Methods

Open publications, conference proceeding, scientific journals, OECD and IAEA documents were used in the review.

## Results

The analyses of fuel ballooning and burst in several countries showed the consideration of the burst of all (100%) fuel during a LOCA event. It is a very conservative approach, since such high damage ratio was not received by any detailed fuel behaviour simulation.

In some countries (Germany, the Netherlands, Switzerland, Argentina) 10% cladding failure is taken into account, but it has to be supported by detailed numerical simulations. The introduction of 33% rate is under discussion in France. The review could not identify any calculated case for PWR reactors above 33% failure rate.

The foreign calculations cannot be used directly for VVER reactors for several reasons:

- The linear heat rate is lower in our VVER-440 reactors than in the typical PWRs. German calculations showed that fuel failure cannot be expected below 400 W/cm<sup>2</sup>, but this value cannot be even reached in our reactors.
- The cladding temperatures in VVERs are low compared to PWRs and this parameter has important effect on burst.
- The different geometry and cladding alloys can also result in significant differences.

It was concluded that on the basis of international practice the 33% failure rate during LOCAs could be introduced, but a more realistic estimation must be supported by detailed thermal-hydraulic and fuel behaviour calculations for several VVER-440 specific LOCA scenarios.

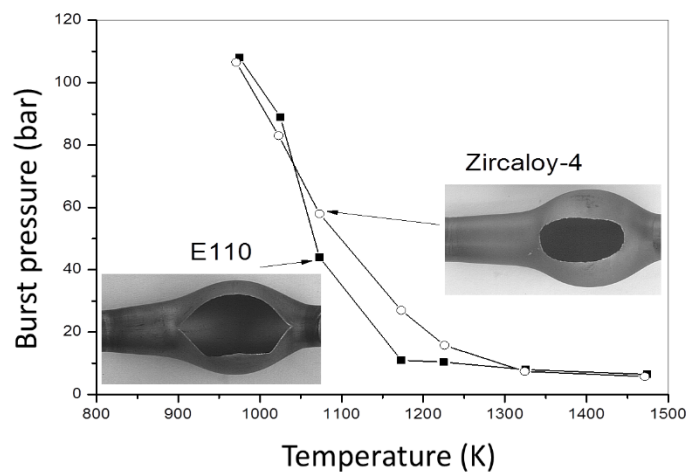


Figure 1: Burst pressure of E110 and Zircaloy-4 cladding tubes

## Remaining work

Series of Paks NPP specific LOCA calculations will be carried out with the FRAPTRAN fuel behaviour code.

## Related publication

P. Szabó, Z. Hózer, E. Slonszki: *Conservative estimation of fuel failure in large break LOCA*, EK-FRL-2014-713-01/01-M1

# DEVELOPMENT OF INTERACTION TECHNIQUES FOR A VIRTUAL CONTROL ROOM

*B. Katalin Szabó, József Páles*

## **Objective**

In an earlier project, a virtual control room (a 3D computer model of the existing plant control room) has been developed for our full-scope simulator of the Paks Nuclear Power Plant, and, in order to make it possible for the user to interact with the simulator, a conventional keyboard-mouse interface and also a user interface for a wireless game console device have been worked out. The goal of the present project was to extend the user interface for touchscreen devices, and to try out modern gesture-driven input devices and assess the feasibility of integrating them into the virtual control room model.

## **Methods**

The 3 touchscreens used in the project are multi-touch infrared overlays over large displays (all manufactured by Samsung). All codes in the project have been written in the Python script language of the Blender 3D modeling tool and game engine.

For handling touchscreen input, following the principle that there should be only one 3D model of the virtual control room, regardless of which input devices (keyboard, touchscreen etc.) are being used, a handler has been worked out to deal with the input coming from the touchscreen. This handler translates touchscreen input into keyboard actions which the existing 3D models of control room devices (pushbuttons, switches) are able to interpret in the same way as if real keyboard keys were pressed. The 3D images of these devices are animated accordingly.

The Leap Motion input device is a new, innovative gesture-based optical device which makes it possible to track the user's hand movements in a relatively precise way. With the help of the SWIG (Simplified Wrapper and Interface Generator) wrapper generator tool, the driver of this device has been interfaced to the Python script of the Blender program. A simple virtual 3D hand model is displayed in the virtual control room, and it is able to follow the movements of the user's hand. The 3D models of buttons and switches have been extended to receive inputs from the Leap Motion (when the virtual hand touches them), but they remain downward compatible with their earlier versions as well.

## **Results**

We have made it possible to manipulate via touchscreen the control room devices in the 3D control room model. In the simulation of pushing the pushbuttons, the user pushes with his finger the image of the pushbutton, this action is detected by the handler, and the simulator is notified of the event. At first, for simulating the turning of the switches in the control room, the standard rotation gesture detection (of Windows 7) was used. However, it did not prove to be reliable enough, sometimes several twisting/turning attempts were necessary to achieve an actual turning of a switch. Therefore, it was decided that these switches would be handled only by tapping gestures, which is a little step backwards in providing a realistic experience, but the reliability compensates for it.

The operation of pushbuttons using the Leap Motion device in the virtual control room has also been achieved. The development is underway for the 3D manipulation of switch devices with the Leap Motion.

## **Remaining work**

We intend to finish the integration of the Leap Motion device. We also wish to refine the 3D hand model for enhancing realism.

A Microsoft Kinect device, capable of tracking the movements of the user in a room, has been interfaced to the Blender program with a demo program which moves a simple "skeleton" according to the movements of the user's body. While tracking is not perfect, the demo justifies the full integration of the device with the 3D model of the virtual control room. We wish to use the Kinect's new V2 model, which is reported to have greater accuracy and better tracking.

We wish to explore the possibilities offered by innovative eyewear (head-mounted displays such as Oculus Rift and Space Glasses) in displaying a 3D model directly in front of the eyes of the user, as a further step towards immersive virtual reality in control room simulation.

# HUNGARIAN SUSTAINABLE NUCLEAR ENERGY TECHNOLOGY PLATFORM

*István Vidovszky*

The Platform was launched in 2010. Its main goal is to influence the agenda of nuclear energy research and development activities in Hungary and to participate in its coordination. The agenda should take into account the needs related to:

- The lifetime extension of Paks nuclear power plant (four VVER-440 units);
- The realization of new nuclear units;
- The closing of the fuel cycle and the development of Generation IV reactors.

Launching the platform is due to the needs and necessities in Hungary, influenced by the European development as well. The above three goals answer the requirements of the nuclear industry and serve as basis for the future development. The lifetime extension of the existing units requires the maintaining of the high safety level reached by now and also should lead to some important further modifications, such as the refurbishment of the process control system. The government's decision concerning new units makes it actual to concentrate on related issues. The strategy concerning the nuclear fuel cycle is one of the hottest issues all over the world.

The platform is represented by MTA EK. The managers of the Platform members form the Governing Board. The Governing Board elaborates the main strategic documents, determines the direction of the activities. Two more bodies were established, the Executive Committee and the Mirror Group. The Executive Committee coordinates the everyday work of the platform, organizes the cooperation with European organizations, is responsible for the work plans and has to organize the conferences as well. Members of the Mirror Group are delegates from those member organizations which are responsible for the determination of the demands for research and development activities. The Mirror Group makes recommendations for the Governing Board aiming to fulfill the Hungarian and international demands and for determining the priorities of the R&D program.

The platform elaborated the detailed strategic research agenda (SRA). Unfortunately, financing of the platform's activities is still not solved. A few tasks which are financed by the Hungarian Atomic Energy Authority and by Paks NPP started in 2014, however the major financing option by the government is still an open issue. There is a realistic hope, that financing of the platform's activities will be solved soon, as the call for proposals was published late 2014, and the platform's proposal has a good chance to win.

# REVIEW OF NEW FUEL TYPES FOR WATER COOLED REACTORS

*Emese Slonszki, Mihály Kunstár, Anna Pintér Csordás, Zoltán Hózer*

## Objective

Literature review was carried out in order to analyse the perspectives of the introduction of new fuel types and to discuss the applicability of them in the currently used thermal reactors.

## Methods

Open publications, conference papers and scientific journals were used as basic sources of the review.

## Results

The review pointed out that the power uprate, the increase of burnup and the introduction of longer fuel cycles in the NPPs can be handled with the currently used fuel composed of UO<sub>2</sub> or MOX pellets and zirconium cladding tubes. The use of burnable poisons and fuel rods with different enrichments, the change of some structural elements of the assembly can fulfill the requirements listed above. However, some specific long term objectives cannot be reached on the basis of the current fuel designs.

In the framework of the present project three new fuel types were reviewed:

- 1) The main objective of the development of **accident tolerant fuel** is the production of cladding materials, whose oxidation under accident conditions would be much lower compared to zirconium alloys. If the intensity of the oxidation could be reduced, it would result in lower temperatures and less hydrogen production. According to some studies, the formation of special non-oxidising layers on the surface of the cladding tubes would significantly reduce the consequences of a reactor accident. The zirconium cladding could be replaced by alternative materials, but that requires the introduction of new cladding production technologies.
- 2) In the **inert matrix fuel** beside the fissile material only such elements are present from which actinides can not be produced. These matrix materials can be in metallic or ceramic form, and different chemical forms of the fissile materials are considered. The inert matrix fuel can be used to decrease the existing plutonium inventories for electricity production in nuclear power plants. Furthermore, using inert matrix fuel, the radiotoxicity of spent fuel can be significantly reduced for final disposal.
- 3) During the application of **dual cooled fuel** the intensified heat removal from the fuel results in the decrease of pellet temperatures. As a consequence, the fission gas release will decrease and the maximum temperatures will be lower compared to normal solid pellets. The potential blockage in the internal channels need further examinations.

The optimisation of composition and construction of the above listed fuel types is in progress in several countries. The in-pile testing of some fuel samples has already been started. The NPP applications of these fuels were analysed by numerical models for different reactor types, including VVERs. However, taking into account the current level of knowledge on these fuel types it is difficult to predict which of them will reach industrial application in NPPs.

Using the combination of the above mentioned three fuel types, such fuel can be produced that would address several objectives: inert matrix, annular pellets and accident tolerant cladding with dual cooling.

## Remaining work

The planned work has been completed. The development of new fuel types will be followed continuously.

## Related publication

E. Slonszki, M. Kunstár, A. Pintér Csordás and Z. Hózer: *New fuel types for water cooled reactors*, EK-FRL-2014-251-01/01 (in Hungarian)

# ASPECTS OF NUCLEAR FUEL UTILISATION UP TO HIGH BURN-UP

*Katalin Kulacsy, Richárd Nagy,  
Nóra Vér, András Vimi*

## Objective

A systematic overview has been prepared covering different aspects of nuclear fuel utilisation up to rod average burn-ups of mostly 70-80 MWd/kgU in order to provide technical support to the Hungarian Safety Authority.

## Methods

Publications available in the open literature and information acquired in the framework of international co-operations in which MTA EK is a member were used to compile studies covering experimental results obtained in research reactors, data derived from operational experience and the possible impact of all these on the fuel operational and safety criteria.

## Results

Burn-up increase has a detrimental effect on the fuel pellet, the cladding, the behaviour of the entire fuel rod and that of the fuel assembly. Continuous improvement in the design aims at minimising this effect.

The **pellet** is affected by continuous swelling caused by fission products. The thermal conductivity of the fuel decreases with burn-up. The rim region of UO<sub>2</sub> pellets starts to re-crystallise at a local burn-up of about 50 MWd/kgU and the high burn-up structure (HBS) is formed. Swelling and local thermal conductivity decrease proceed in the HBS as well, but at rates lower than that seen in the fuel keeping its original structure. The HBS is characterised by a smaller Young's modulus than the original fuel, i.e. the HBS is softer. An important area for improvement is the introduction of additives. Increasing fuel grain size by e.g. chromia doping is promising regarding both fission gas release and pellet-cladding mechanical interaction.

Oxidation and hydrogen absorption of the **cladding** outer side proceed not so much with burn-up as with in-reactor time and temperature. Alloys containing niobium resist oxidation better than those containing tin. Due to the mechanical interaction occurring in normal operation between the fuel and the cladding, the HBS and the oxide formed after gap closure on the inner side of the cladding (due to the oxidising effect of the fuel) may penetrate into each other more and more as burn-up increases: strong bonding may arise between the pellet and the cladding. Modern cladding materials are either improved (E110, Zircaloy-4 and ZIRLO) or new (MDA, M5) or coated and/or lined.

The release rate of noble gases and volatile fission products to the **rod's** free volume increases above a rod average burn-up of about 40 MWd/kgU, even at low temperatures (athermal release). The threshold temperature (and rating) at which high-temperature (thermal) release is enhanced beyond 1% decreases with the increase of burn-up. Among the volatile fission products, iodine may be the principal cause of cladding inner side corrosion, eventually leading to crack initiation. Alloys containing niobium are less susceptible to such corrosion.

Among the deformations of the fuel **assembly**, bowing and twisting are the most important issues, as these may cause incomplete control rod insertion. New mechanical designs aim at stabilising the geometry.

Despite all the efforts of fuel manufacturers, failures still occur. Known fuel failures occurring during normal operation that still deserve attention are fretting, manufacturing defects, pellet-cladding interaction and corrosion and hydriding, possibly together with crud formation. Fuel failure rates have decreased during the past decades. The reliability indices of the fuel for VVER-440/213 are outstanding among VVER fuels.

As far as **criteria** are concerned, several burn-up dependent operating limits and safety criteria (cladding stress and strain, PCI (Peripheral Component Interconnect), cladding lift-off, fuel melting) can be formulated in terms of a burn-up dependent linear heat generation rate limit curve for normal operation and anticipated operational occurrences.

Oxidation and hydriding during operation may cause the degradation of cladding mechanical properties. For modern alloys, such as E110, oxidation and hydriding remain low and the cladding remains ductile even at high burn-up (long dwelling time in the reactor). This is also important for fuel failures during LOCA (Loss-of-Coolant Accident) and RIA (Reactivity Initiated Accident). Oxidation during base irradiation and during the transient can be added up (conservative approach) and the total oxidation can be required to remain below the 17% ECR (Equivalent Cladding Reacted) limit. Cladding embrittlement due to hydrogen uptake may influence accident failures, burn-up dependent enthalpy and oxidation limits may therefore be introduced for RIA and LOCA, respectively, especially for claddings prone to significant hydrogen uptake.

Fuel fragmentation, relocation and dispersal (FFRD) may occur during RIA and LOCA. The enthalpy increase limit for RIA prevents fuel dispersal. FFRD for high burn-up fuel during LOCA is currently under investigation. The regulatory approach is likely to be a limit of the power output of high burn-up fuel assemblies, which is usually fulfilled anyway by core design.

## Remaining work

The work has been completed.

## Related publication

K. Kulacsy, R. Nagy, N. Vér, A. Vimi: *Establishing the utilisation of high burn-up fuel*, EK-FRL-2014-281-01/01 (2014), in Hungarian

# ISOTOPES DISSOLUTION DURING WET STORAGE OF DAMAGED AND LEAKING VVER FUEL WITHIN THE FIRST-NUCLIDES PROJECT

*Emese Slonszki, Zoltán Hózer, Péter Szabó*

## Objective

The 3-years FP7 Collaborative Project FIRST-Nuclides (Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel) aims to provide new and comprehensive knowledge of the fast release of safety relevant radionuclides from light water reactors, spent nuclear fuel after failure of the canister in an underground repository. The objective of MTA EK contribution to Work Package 1 in the framework of FIRST-Nuclides project is the characterization of VVER fuel [1],[2], while to WP3 is the determination of dissolution rates for several isotopes from damaged and leaking VVER fuel assemblies stored in water for several years [4],[5]. The participation of MTA EK in this project was supported by National Research, Development and Innovation Found (NKFIA) (contract No.: EU\_BONUS\_12-1-2012-0033).

## Methods

The main characteristics of the damaged and leaking VVER-440 fuel assemblies have been collected. There were no special examinations of the fresh fuel assemblies before loading them into the reactor core, for this reason factory data were used to characterize the fuel. The operational parameters were derived using power histories of from the NPP. The calculations were carried out with fuel behaviour codes FUROM and TRANSURANUS. The isotope inventories were determined taking into account the real power histories of each fuel assembly for almost one thousand isotopes.

The dissolution rates were different in the two evaluated conditions which are attributed to the pH. There were two series of measurements at Paks NPP that can be used for the evaluation of fuel dissolution in wet environment:

1. Thirty fuel assemblies were damaged at the power plant during a cleaning tank incident in 2003, which were then stored in a special service area of the spent fuel storage pool for almost four years. Based on the continuously measured activity concentrations, we could calculate release rates for several isotopes.
2. A leaking fuel assembly was identified at the NPP in 2009. The assembly was removed from the reactor core and then placed in the spent fuel storage pool. A special measurement programme was carried out in the spent fuel storage pool to investigate the activity release from the leaking fuel rod at wet storage conditions. The data from this programme was used for the calculation of dissolution rates.

## Results

Within the FIRST-Nuclides project, dissolution rates of several isotopes from VVER fuel were determined for two pH in the coolant based on activity measurements at Paks NPP. The present work summarizes both the design and operational characteristics of fuels and the calculation methods and dissolution rates of isotopes during and after the incident of Unit 2 of Paks NPP in case of 11 isotopes and during the wet storage of a leaking fuel assembly of Paks NPP in case of 7 isotopes. Dissolution rates of  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$ ,  $^{125}\text{Sb}$  and  $\text{UO}_2$  were determined in both situations. The release ratio of these isotopes and  $\text{UO}_2$  from VVER fuels were in good agreement with the data that were originated from the hot cells examinations which were carried out in this project. The results of this project may represent the good base for designing of domestic deep geological repository.

## Remaining work

The expected completion of this project is the end of this year. In connection with a new tender based on the results of this project there are ongoing negotiations with foreign partners.

## Related publications

- [1] Z. Hózer, E. Slonszki: *Characterisation of spent VVER-440 fuel to be used in the FIRST-Nuclides project*, EK-FRL-2012-421-01/01
- [2] Z. Hózer, E. Slonszki: *Characterisation of spent VVER-440 fuel to be used in the FIRST-Nuclides project*, 1st Annual Workshop Proceedings of the Collaborative Project "Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides), Budapest 09 - 11 October 2012, Bernhard Kienzler, Volker Metz, Lara Duro, Alba Valls (eds.), pp. 87-101, <http://dx.doi.org/10.5445/KSP/1000032486>
- [3] Slonszki Emese, Hózer Zoltán, Szabó Péter: *Aktivitás-kikerülés a fűtőelemekből mélygeológiai tárolóban. [in Hungarian] FIRST-Nuclides projekt*: Nukleon, VII/2, 158 (2014. május)
- [4] E. Slonszki, Z. Hózer: *Determination of dissolution rates for damaged and leaking VVER fuel stored in water*, EK-FRL-2013-421-01/01-M1
- [5] E. Slonszki, Z. Hózer: *Determination of dissolution rates for damaged and leaking VVER fuel stored in water*: 2st Annual Workshop Proceedings of the Collaborative Project "Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides), Antwerp 05 - 07 November 2013, Bernhard Kienzler, Volker Metz, Lara Duro, Alba Valls (eds.), pp. 155-162, <http://dx.doi.org/10.5445/KSP/1000041743>
- [6] E. Slonszki, Z. Hózer: *Isotopes dissolution during wet storage of damaged and leaking VVER fuel*, EK-FRL-2014-421-01/01



# ACCESS TO SEVERE ACCIDENT FACILITIES IN THE EU SAFEST PROJECT

*Zoltán Hózer, Imre Nagy, György Ézsöl, Attila Guba*

## Objective

The main objective of the SAFEST project in 2014 was to carry out EU-supported calls and allow user access to SAFEST infrastructure for severe accident research.

## Methods

MTA EK experts contributed to the writing of the rules of access to SAFEST facilities with the specification of the available Hungarian facilities.

## Results

Two severe accident facilities were offered for international access:

- The CODEX (COre Degradation EXperiment) facility was built for the investigation of early phase severe accident phenomena with electrically heated bundles. Several experiments have been performed with VVER and PWR type fuel rods. After the experiments the post-test examinations of the bundle are carried out with several techniques, including metallography, SEM (Scanning Electron Microscopy) and microprobe analysis.
- The CERES facility was built for the experimental modelling of the cooling loop to be implemented to remove heat from a VVER-440 reactor vessel in the late phase of a severe accident. The scaling ratio of CERES is 1:40 for the external surface of reactor vessel and 1:1 for the elevations to provide driving forces for the natural circulation.

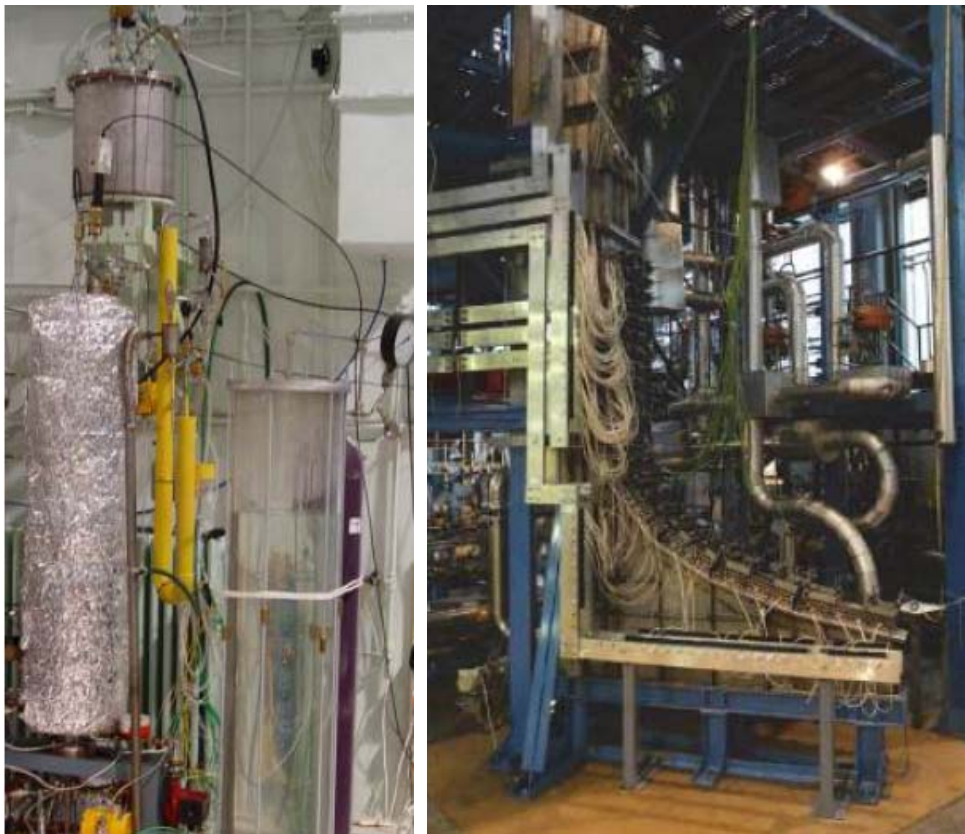


Figure 1: View of the CODEX (left) and CERES (right) facilities

## Remaining work

Severe accident experiments will be performed on the CODEX and CERES facilities according to the requests of foreign partners.

## Related publication

A. Miassoedov, C. Journeau, S. Bechta, D. Grishchenko, Z. Hózer, D. Bottomley, D. Manara, M. Kiselova, G. Langrock, M. Fischer, P. Piluso and M. Schyns: *Rules of access to SAFEST facilities*, SAFEST-DRI-D3.1 (2014)



# PREPARATION FOR THE RECONSTRUCTION OF VERONA CORE MONITORING SYSTEM

*Gábor Házi, Csaba Horváth, József Páles, Gábor Boleska, Tamás Fogd*

## Objective

Paks NPP plans to extend the length of fuel cycles to 15 months from 12 by introducing a new type of fuel assemblies. As a consequence of this plan, the VERONA core monitoring system has to be upgraded, improving the accuracy of the reactor core physics calculations and taking into account the new, a bit more complex composition of the fuel. The amount of computations needed in the new reactor physics calculations will significantly increase, therefore the existing algorithms have to be accelerated. Since both the hardware and software components of VERONA system are somewhat obsolete, Paks NPP decided to refurbish the overall core monitoring system besides the development of the reactor physics calculations.

## Methods

In 2014 Paks NPP initiated some pilot projects to establish the reconstruction of VERONA system, focusing on the solution of the following problems:

- the existing reactor physics calculations have to be improved and accelerated - RPH (reactor physics) pilot project,
- a new module has to be integrated into the system, which can aid the operators to plan power transient actions taking into account all operational margins - VETRAN (VERona TRANsient) pilot project,
- an overall plan has to be prepared for the refurbishment
  - proposing new hardware components,
  - refreshing the software modules,
  - simplifying the local VERONA network,
  - introducing the application of virtualization technology,
  - replacing the currently used iFIX SCADA solution,
  - eliminating some known deficiencies of the system,
  - etc.

## Results

In the RPH pilot project the existing reactor physics calculations were restructured and some algorithms have been heavily parallelized using a high performance Tesla graphics processing unit (GPU) [1]. The new algorithms will be verified and validated in the spring of 2015, using the VERONA-t (test) configuration, which is a test bed for VERONA system modifications. It can be driven by the core measurements of any unit of Paks NPP and the results of new reactor physics calculations can be compared with the old ones.

In the VETRAN pilot project a prototype of the transient planner module has been developed, designing a specific user interface for the module [2]. The new module has been coupled with the full-scope simulator of Paks NPP and the instructors of the simulator tested its accuracy and studied the viability of the user interface. According to the instructors' proposal, the new module has been improved gradually achieving finally that all instructors gave a good merit rating for the new module.

In 2014, a technical specification was also prepared to establish the reconstruction of the overall core monitoring system [3], proposing:

- new hardware components,
- strategy for the replacement of obsolete codes and for the introduction of virtualization,
- a new local network structure with components conform with the recently renewed technological computer network of Paks NPP,
- a solution for the replacement of iFIX using SIMTONIA (SIMulation TOols for Nuclear Industrial Applications) framework developed by MTA EK,
- etc.

## Remaining work

Based on the technical specification, the new system has to be developed. This work has already been started in December of 2014. The new system will be partially installed first in the second unit of Paks NPP in autumn of 2015 and the project will be finished with the installation at the last unit in 2017.

## References

- [1] Z. Kálya, I. Pós, G. Házi, *VERONA 7.0 Reactor Physical Calculations – System Design*, DAR: 000000I01872-KFA, 2014, (in Hungarian)
- [2] G. Házi, J. Páles, *Computer aided transient design for operators – System Design*, EK-RMSzL-2014-739-00/01, DAR: 000005J00005-KFA, 2014, (in Hungarian)
- [3] Cs. Horváth, J. Páles, G. Fazekas, Cs. Korponai, L. Szunemán, L. Varga, V. Vörös, *VERONA 7.0 Technical Specification, Vol. 1*, EK-RMSzL-2014-703-00/01, DAR: 000000I01729-KFA, 2014, (in Hungarian)

# EFFECT OF LONGER CAMPAIGN PERIODS ON THE PRIMARY COOLANT ACTIVITIES AND DOSIMETRY CONDITIONS

*Emese Slonszki, Zoltán Hózer, Tamás Pázmándi, Péter Szántó, György Pátzay (BME KKFT), Emil Csonka (BME KKFT)*

## Objective

The main objective of the work was the estimation of the effect of introduction new fuel with higher enrichment and extension of fuel campaign to 15 month (from the currently used 12 month period) on the dosimetry conditions in the vicinity of primary loops of Paks NPP.

## Methods

The primary coolant fission product activities were determined taking into account of leaking fuel rods.

The effect of surface contamination was estimated with the assumption that the mass of deposited materials increased proportionally with the period of the campaign.

The analyses covered several measured activation products ( $^{51}\text{Cr}$ ,  $^{54}\text{Mn}$ ,  $^{58}\text{Co}$ ,  $^{59}\text{Fe}$ ,  $^{60}\text{Co}$ ,  $^{95}\text{Nb}$ ,  $^{95}\text{Zr}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{124}\text{Sb}$ ) and fission products ( $^{103}\text{Ru}$ ,  $^{131}\text{I}$ ,  $^{134}\text{Cs}$ ,  $^{136}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{140}\text{La}$ ,  $^{144}\text{Ce}$ ). The measured data for two years of NPP operation were evaluated, including normal operation, shut-down and start-up conditions. The activity concentrations during reactor operations without water purification system were also evaluated.

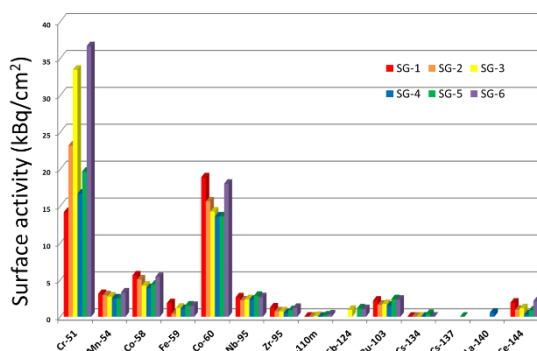


Figure 1: Surface activity components on six steamgenerators

Special models have been developed for the simulation of fission product accumulation in different components. .

## Results

The results of the calculation indicated some increase of primary coolant activity concentrations and doses in the rooms around primary circuit components due to the increase of campaign period from 12 to 15 month. However, the analyses of the data pointed out that this estimated increase is negligible in comparison with the scatter of measured data from different NPP units.

The longer campaign will result in the production of more fission products, but it has only small effect compared to those from the current campaign period. The maximum allowable activity concentrations will not change with the introduction of new campaign period and can be easily maintained with the water purification system. So even if a high burnup fuel will leak, the activity concentrations can be kept below the limits.

The series of executed calculations pointed out that the following effects have more important impact on the activity concentrations, surface contamination, doses of the filters and doses in the rooms close to primary circuit components than the length of campaign:

- presence and number of leaking fuel rods in the core,
- period of reactor operation with leaking fuel rods,
- mass of tramp uranium on the core surfaces,
- water purification system flowrate,
- frequency of the change of ion exchanger filters.

## Remaining work

The planned work was completed.

## Related publication

E. Slonszki, Z. Hózer, T. Pázmándi, P. Szántó, Gy. Pátzay E. Csonka: *Analysis of the activity accumulation on the primary coolant filters related to the extension of fuel campaigns*, EK-FRL-2014-704-01/01 (in Hungarian)

# VALIDATION OF THE KARATE CODE SYSTEM AGAINST THE LATEST OPERATIONAL DATA AND STARTUP MEASUREMENTS

*András Keresztúri, György Hegyi, Emese Temesvári, Lajos Korpás*

## Objective

In the last decades, KARATE-440 was elaborated and developed continuously to calculate VVER-440 reactor cores by coupled neutron physical-thermo-hydraulics models. The main goal of the calculations is the core reload design, however, certain safety analyses amenable to a static code can be analyzed also by KARATE-440. The program serves economic core reload design so that the limitations demanded by the safety analysis should be observed. The latter function is utilized for the periodic independent check of the Paks NPP core design. On the other hand, in the last years several modifications of the VVER fuel construction and the corresponding core design aiming at more economic fuel utilization - like for example Gd doped fuel - were introduced by Paks NPP which made further development of the models necessary. Having regard to the above situation, continuous validation from year to year against the latest operational and start-up measurements is indispensable for the establishment of the uncertainties and the margins for the calculated safety related frame parameters. In 2013, the cycles of Paks NPP finished in 2012 were used for the validation. An additional task was the adaptation of the KARATE modules to the more modern INTEL FORTRAN environment.

## Methods

Model validation, comparison of the calculated and measured data

## Results

The following parameters were used for the validation

- core burnup dependent radial peaking factors based on the assembly-wise in-core temperature rises,
- core burnup dependent operational critical boron concentrations,
- critical boron concentrations measured at the Minimum Controllable Power,
- moderator temperature reactivity coefficients measured at the start-up procedure,
- integral and differential efficiencies of the control rod groups.

According to the validation results, there are no significant changes of the deviations from the measurements as compared to the earlier cycles. As an example, Fig. 1 shows the comparison of the measured and calculated differential control rod group worth for Unit 3 using high enriched Gd doped fuel. The deviation is about 10 %, which is in the range of the measure scattering. The GLOBUS module of the KARATE code system was successfully adapted to the INTEL FORTRAN environment.

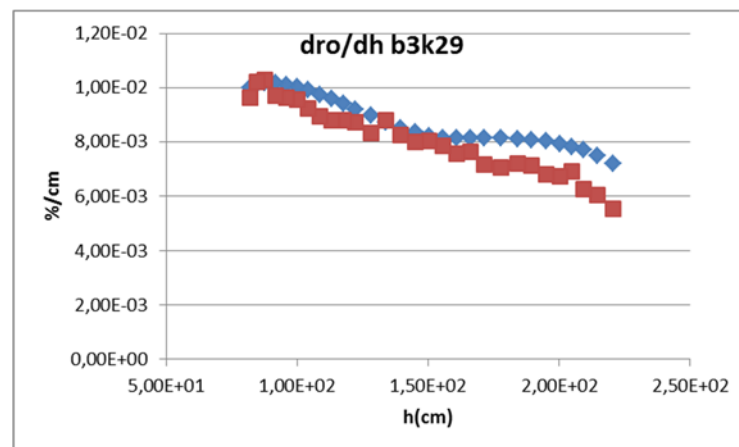


Fig. 1: Measured (lower curve) and calculated differential controls rod worth for Cycle 29 of Unit 3 depending on the control rod axial position ("h")

## Remaining work

Adaptation of the SADR KARATE module to the INTEL FORTRAN environment

## Related publications

- [1] Gy. Hegyi, L. Korpás: *Comparison of the KARATE 5.0 results with the measurements and C-PORCA calculations for the last realized cycles of Paks NPP*, in Hungarian, MTA-EK-RAL-2014-706/1-M0.
- [1] Gy. Hegyi, E. Temesvári: *Adaptation of the GLOBUS KARATE module to the INTEL FORTRAN under Windows7 environment*, in Hungarian, MTA-EK-RAL-2014-706/2-M0.

# STRUCTURAL INTEGRITY CALCULATIONS OF VVER440 V213 REACTOR PRESSURE VESSELS AT NPP PAKS

*Tamás Fekete, Levente Tatár, Dániel Antók*

## Objective

The Reactor Pressure Vessel (RPV) is one of the most important components for safety and lifetime of a Nuclear Power Plant (NPP), accidental failure of which may cause serious environmental damages. RPVs have large cross-sections (VVER-440 V213: 149 mm wall thickness with 3800 mm diameter); work at elevated temperatures ( $\approx 270 - 290^\circ\text{C}$ ) and high pressures ( $\approx 12.2\text{ MPa}$ ). The most important functions of the RPV are the maintenance of pressure and temperature conditions, which are necessary for controlled power generation during operation, heating-up and cooling-down of the reactor, cooling-down of the core under emergency conditions and preventing release of radioactive materials into the containment. These requirements mean that the vessel should keep its integrity during its lifetime, taking into account all possible modes of operation. Structural integrity calculations are tools to analyse mechanical behaviour of the RPVs under the influence of various loading cases. The goal of structural integrity calculations is the assessment of safety limits of RPVs for all defined loading cases. Two types of loading cases are relevant for the fracture mechanics based structural integrity calculations: normal operation conditions and postulated accident situations leading to Pressurised Thermal Shock (PTS). For normal operation, the start-up and shutdown processes, as well as pressure testing situations have to be assessed. These calculations lead to the construction of  $p$ - $T$  limit curves that are valid during the operation of the RPV. PTS phenomenon can occur when in some accidental situations extra quantity of cooling water flows into the RPV, causing severe overcooling of the vessel wall. A PTS event can cause a dangerous situation regarding the structural integrity of RPVs, as high thermal gradient develops through the vessel wall, causing high thermal stresses, which are superposed to stresses originating from internal pressure. The thermal and stress fields in RPVs are very complex, caused partly by complexity of the pressure vessel geometry itself, and partly by the complex thermal loadings. The main goal of PTS calculations is to assess allowable service time of the RPVs from PTS point of view. During last years Paks NPP developed a strategy for introduction of a new generation of fuel elements that could affect ageing of structural materials and allowable service time of the RPVs therefore. The goal of the project was a complete reassessment of allowable service time and  $p$ - $T$  limit curves of the VVER 440 V213 type RPVs installed at NPP Paks.

## Methods

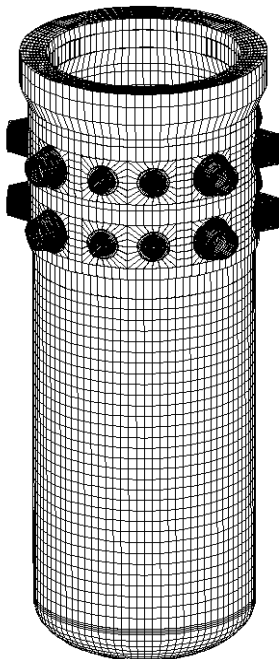


Figure 1: Model of VVER-440 RPV

The methodology of structural integrity calculations for normal operation was developed by MTA EK. At first, coupled 2D temperature field and linear elastic stress field calculations had been performed for the lower cylindrical part of the vessel for start-up and shutdown conditions. The stresses included thermal stresses resulting from the start-up and shutdown transients, as it is prescribed in national guidelines. Fracture mechanics calculations were based on the linear elastic fracture mechanics theory. The postulated defects were surface breaking flaws. The  $p$ - $T$  limit curves of the reactor pressure vessel had been derived from results of fracture mechanics analyses and critical temperatures of brittleness ( $T_k$ ) curves of aged structural materials. Critical temperatures of brittleness curves of RPVs had been derived from results of Charpy impact measurements performed in the frame of surveillance program of the RPVs.

For PTS structural integrity calculations, the methodology was developed by MTA EK. At first, detailed neutron fluence calculations were performed to provide input for the assessment of material ageing of irradiated parts of the RPVs. In a second stage, system thermo-hydraulics calculations had been performed to provide thermal boundary conditions for the structural integrity calculations. For fracture mechanical structural integrity calculations a hybrid methodology had been developed. In first step of the calculations 3D finite element temperature field, linear elastic stress field calculations had been performed for the body of the vessel and for the nozzles taking into account all transients analysed by system thermo-hydraulics calculations. In the second step, fracture mechanics calculations, based on linear elastic fracture mechanics (LEFM) were performed using analytical formulas.

## Results

During the first part of the project, neutron fluence calculations and system thermo-hydraulics calculations had been performed resulting in updated reassessment of allowable service time of RPVs and the  $p$ - $T$  limit curves of the vessels.

In the second part of the project, PTS structural integrity calculations and analyses for constructing the  $p$ - $T$  limit curves were performed. The results showed that allowable service time of the RPVs is higher than the planned extended lifetime in case of the new generation of fuel elements.

# POST-TEST CALCULATIONS OF EXPERIMENTS PERFORMED ON E110 AND E110G CLADDING WITH THE CODE FRAPTRAN

*Katalin Kulacsy, Márton Király*

## Objective

Many separate effects tests have been performed on the Russian cladding material E110, and some on its improved version E110G, both at AEKI (the predecessor of MTA EK) and abroad. In order to extend the validation of the transient fuel behaviour simulation code FRAPTRAN, a number of such tests were simulated and the results were evaluated. The work was supported by Paks NPP.

## Methods

The following tasks were performed:

- the isothermal ballooning and burst tests performed at AEKI were simulated to validate the mechanical models of the code,
- the cladding material properties functions built into the code were compared to experimental data where available (no data were found for E110G),
- the built-in kinetics for oxidation in high-temperature steam were compared to the results of the AEKI oxidation tests; new measurements were made in order to fill in the gap where kinetics change dramatically and no data were available.

## Results

The mechanical behaviour was reproduced well by the code calculations, although the scatter of the relative deviations was rather high. The alloy E110G showed a little higher strength than E110, but the difference was not significant.

The material properties functions agreed well with the available measurements (found only for E110, but E110G is expected to exhibit similar behaviour).

The most important difference between the alloys E110 and E110G is their oxidation kinetics in high-temperature steam: while E110 oxidises rather rapidly, furthermore it exhibits breakaway oxidation (the oxide layer is not compact but peels off in scales, allowing a fresh metal surface to oxidise) within a certain temperature range, E110G oxidises a little faster and produces a compact oxide layer at all tested temperatures and oxidation times. The code FRAPTRAN includes a best-estimate and a conservative oxidation kinetic correlation, both fitted to Zircaloy data. The best-estimate correlation was found to be rather conservative even for E110, except for the breakaway regime, and very conservative for E110G, new correlations were therefore fitted to the data measured at AEKI. Three correlations were established and implemented in the code FRAPTRAN: a best-estimate correlation for E110 (together with a breakaway limit), a best-estimate and a conservative correlation for E110G. The results for the AEKI tests on E110G samples are shown in Fig. 1.

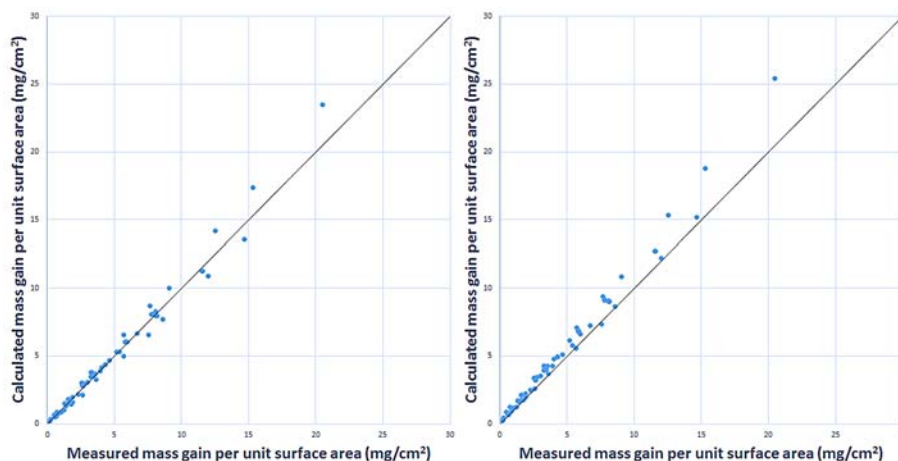


Figure 1: Comparison of calculated to measured weight gain per unit surface area for the E110G alloy: best-estimate correlation (left) and conservative correlation (right)

## Remaining work

The work has been completed.

## Related publications

- [1] K. Kulacsy: *Post-test calculations of ballooning tests performed with the old (E110) and the new (E110G) claddings by the code FRAPTRAN*, EK-FRL-2014-712-01/01, in Hungarian
- [2] K. Kulacsy, M. Király, E. Perez-Feró: *Oxidation kinetics of E110 and E110G in high-temperature steam*, EK-FRL-2014-712-01/02, in Hungarian

# THE MEASUREMENT OF THE MECHANICAL PROPERTIES OF E110 AND E110G ZIRCONIUM ALLOY CLADDING TUBES

Márton Király, Márta Horváth, Zoltán Hózer, Richárd Nagy, Imre Nagy,  
Tamás Novotny, Erzsébet Perezné Feró, Gábor Uri, Nóra Vér

## Objective

The purpose of the work was to determine the ultimate tensile strength of the E110 and E110G cladding tubes and to assess the differences between these alloys.

## Methods

Tensile tests were carried out on both alloy tubes using two-winged axial and short ring test samples. The tensile samples were prepared by CNC milling and slow cutting. The ring and axial tensile tests of the samples were carried out by Instron 1195 universal testing machine, the load-displacement curves were recorded and evaluated. These tensile tests were performed at ambient, elevated (150 °C) and expected in-service (300 °C) temperatures on as-received, oxidised (1-2,8% Equivalent Cladding Reacted, ECR) and hydrogenated (100-400 ppm absorbed hydrogen content) axial and ring cladding samples of both alloys. The oxygen and hydrogen pickup of the samples was calculated by their weight gain. The oxidation was limited to 800 °C and 2,8 ECR% to avoid breakaway oxidation and to keep the surface of the samples intact.

We have set up an instrumented furnace to observe the thermo-mechanical creep of the cladding tubes at 500 °C temperature and 5-10 MPa inner pressure over a period of a few months. To the ends of the 100 mm long cladding tubes a plug was welded, and the tubes connected to these plugs were pressurized with high purity argon. The diameter change of the samples was registered by laser micrometer at different angles, the length change was measured with digital calliper.

## Results

The ultimate tensile strength of the E110G cladding samples at ambient temperature was 11% higher than that of the E110 samples in both axial and hoop direction, although this difference was smaller for lower temperatures. For both alloys the ultimate tensile strength in the hoop direction was about 6% lower than the axial one. The chemical treatments caused only minor changes to the tensile strength, 2,8 ECR% oxidation raised the tensile strength of the samples by 20 MPa, while 400 ppm hydrogen content lowered it by 10 MPa for both alloys.

The creep specimens pressurized at 7,5 and 10 MPa at 500 °C have failed after just a few days, only the ones pressurized at 5 MPa could be measured for longer periods of time. All stages of the creep curve could be observed on these samples that eventually failed after 56 days. Due to the different wall thickness of the two cladding tubes the results were inconclusive, but were very similar for both alloys, further measurements will be conducted on the samples.

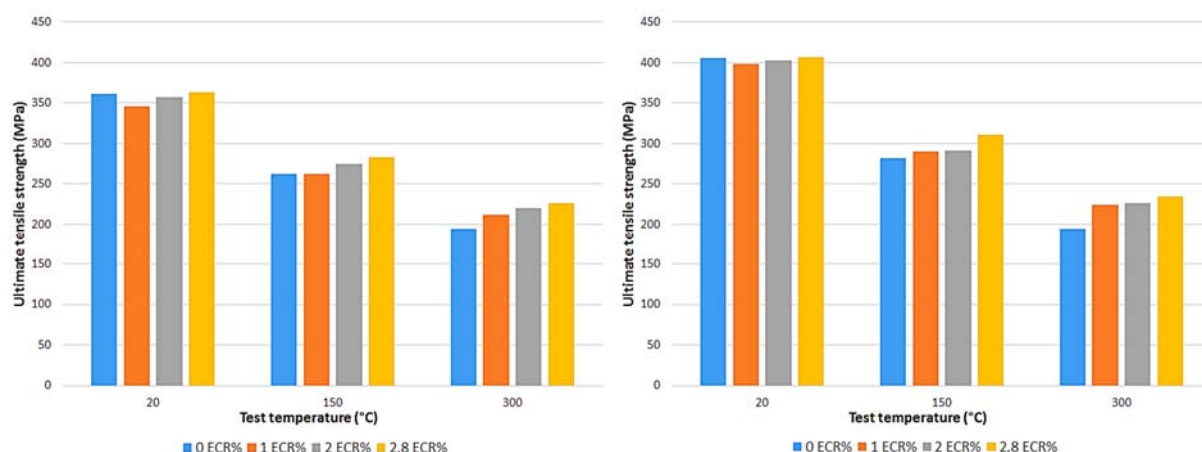


Figure 1: The measured ultimate hoop tensile strength of the E110 (left) and the E110G (right) claddings at different temperatures after 0-2,8 ECR% oxidation

## Remaining work

The hydrogenated axial samples were not yet prepared, their tensile tests will be carried out in early 2015. The project will continue in 2015 with metallography of some samples to determine the exact oxide layer thickness and the measurement of the anisotropy of the cladding tubes using neutron diffraction.

We will also measure the thermo-mechanical creep of the cladding tubes at 300 °C temperature using a different setup.

## Related publication

M. Király, L. Horváth, Z. Hózer, R. Nagy, I. Nagy, T. Novotny, E. Perez-Feró, N. Vér: *Investigation of the ultimate tensile test and creep behavior of E110G cladding*, EK-FRL-2014-718-01/01 (in Hungarian)

# UPDATING THE FINAL SAFETY ANALYSIS REPORT OF NPP PAKS

*András Keresztúri, Attila Guba, Tamás Pázmándi*

## **Objective**

In the near future, a new fuel assembly type enriched to 4.7 % is foreseen to be introduced at Paks NPP (Nuclear Power Plant) allowing more economic 15 month equilibrium fuel cycle length. The application of the new assembly modifies the power distributions essentially on all geometry scales: namely the distribution in the fuel pellet, the pin-wise and the assembly-wise distributions. The reloading schemes are modified to a great extent, too. The relevant parts of the Design Basis Analyses – where modified distributions are important – were repeated. Additionally, the subcriticality of the transport and storage devices of the NPP was investigated by using an advanced burnup credit methodology. The Chapters 4 and 15 had to be updated for the licensing project.

## **Results**

The Chapters 4 and 15 were supplemented with the results of the following analyses:

- Steam line break
- Inadvertent closure of 6 MSIV (Main Steam Isolation Valve)
- Seizure of one MCP (Main Coolant Pump)
- Inadvertent withdrawal of a control rod group
- Control rod ejection
- Stuck control rod in upper and lower position
- Inadvertent connection of one closed loop
- Large break LOCA (Loss of Coolant Accident)
- Erroneous loading of one fuel assembly
- Erroneous loading of one fuel pin
- Inadvertent withdrawal of a control rod group without scram

For checking the fulfillment of the PCI (Pellet Clad Interaction) requirement, the following analyses were performed

- Loading up to the nominal power after refueling
- Operation in the 100-0-100 % power range
- Operation in the 100-50-100 % power range
- Variation of the power in the 10 % range
- Inadvertent opening of one closed loop
- Control rod withdrawal
- Environment dose estimations for the large break LOCA using the conservative isotopic inventory
- Dose estimations of the transport and storage devices in case of abnormal events
- Thermo-hydraulic analysis of the spent storage pool

## **Remaining work**

There is no remaining work.

## **Related publications**

Proposed preliminary versions of Chapters 4 and 15 of the FSAR



# SURET - A SUBCHANNEL MODEL FOR VERETINA CORE ANALYZER

G. Házi

## Objective

The objective of this work was to extend the applicability of VERETINA core analyzer system with thermohydraulic analysis in the level of subchannels.

## Methods

A new model called SURET (SUBchannel module for RETina) has been developed. The governing equations of this model are the subchannel mass, momentum and energy conservation equations of the coolant. Regions between the fuel rods of a fuel assembly are divided into small portions in radial directions (subchannels) and the mass, momentum and energy transfer mechanisms between the subchannels are taken into account by mechanistic or specific models. Uniform discretization is used in axial direction for each subchannel. The discretized equations are solved by an explicit method. Lateral mixing between subchannels (and between shroudless fuel assemblies) can be simulated with a specific model.

## Results

In 2014, the model development of SURET has been finished and some preliminary calculations have been performed verifying the convergence of the numerical algorithm. Calculations have been performed studying a single fuel assembly and a set of shroudless assemblies (7 assemblies coupled with each other). Furthermore, software tools have been developed to support the validation process of the simulation results in the future (e.g. tool to support the comparison of SURET's simulation results with the ones of COBRA). As an example, simulation results of SURET are shown in Fig. 1. In this calculation the assembly is heated by the central rods as one can see on the left. The corresponding temperature distributions are shown in the center and on the right as the coolant moves towards the outlet of the channel. The distributions are symmetric as it is expected and spread out in the lateral direction due to lateral mixing. The coolant temperature is gradually increasing as the coolant approaches the outlet.

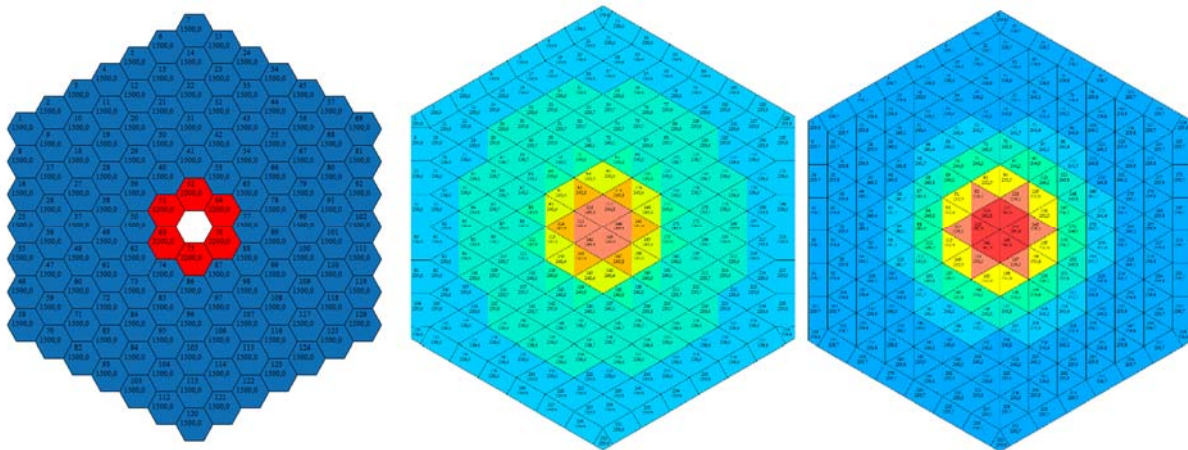


Fig. 1: Results of SURET's calculations. Centrally heated rod (left) and the corresponding temperature distributions in various axial levels (center and right).

## Remaining work

SURET has to be validated using simulation results obtained by other subchannel codes (e.g. COBRA) and/or measurements. Both single assembly and core calculations have to be performed. It would also be desirable to speed up the calculations using Graphics processing unit accelerated numerical algorithms.

## Related publications

- [1] G. Házi, SURET – Subchannel calculations in the RETINA system – System Design, EK-RMSzL-2013-726-00/02, 2014 (in Hungarian)
- [2] G. Házi, SURET – Subchannel calculations in the RETINA system – Verification and Valiation, EK-RMSzL-2013-726-00/03, 2014, (in Hungarian)
- [3] G. Házi, SURET – Subchannel calculations in the RETINA system - Core modeling, EK-RMSzL-2014-726-04/01, 2014, (in Hungarian)



# ANALYSES OF BEYOND DESIGN BASIS ACCIDENT HOMOGENEOUS BORON DILUTION SCENARIOS

*András Keresztúri, György Hegyi, Csaba Maráczy, István Trosztel*

## Objective

Boron dilution events can lead to serious consequences in Pressurized Water Reactors (PWRs) - including the VVER type - without applying countermeasures. Thanks to the appropriate measures the probability of such events is extremely low even in case of the VVER-440 type where Main Isolation Valves are in the primary loop. At Paks NPP, the corresponding PSA studies proved that such events with not negligible probability can lead only to so-called homogeneous dilution. According to the probability data, the contribution of the boron dilution scenarios is about 25% to the Core Damage Frequency originating from the internal events (including both the shut down and the nominal power states) supposing in the present PSA that all of them are leading to core damage. Nevertheless, the question can be raised whether this assumption is valid or not. The goal of the investigations of the presented activity was just to answer this question.

## Methods

Safety analyses by using the coupled KIKO3D-ATHLET code. Best estimate calculations are appropriate for analyzing the BDBA scenarios, nevertheless it was necessary to take into account the variability of the initial conditions which is caused by the different reloading schemes regarding also the supposed future core configurations. Therefore, enveloping values of the following determining reactor physics parameters influencing the recriticality and further power rise were used:

- Reactivity reserve (for burnup, power rise and heat up)
- Minimum (most negative) boron concentration reactivity coefficient
- Minimum worth of shut down rods
- Maximum (least negative) moderator temperature reactivity coefficient

The impact of two further parameters – namely the strength of the spontaneous fission source determining the flux level before the transients, moreover, the initial primary coolant temperature – was not trivial. Therefore a sensitivity analysis on their influence had to be performed. It turned out that the strength of the spontaneous fission source in the reasonable range has negligible effect on the power rise after the recriticality, while transients starting from lower coolant temperature are leading to more disadvantageous results.

## Results

Without the presented analyses of homogeneous boron dilution events, their significant contribution to the CDF had to be assumed in the PSA analyses. Nevertheless, the analyses have shown that the homogeneous boron dilution events don't lead to core degradation, although large amount of steam can be generated in the primary and in the secondary loops in case of absence of any reactivity protection. In spite of the very slow dilution, the time dependent boron concentration is becoming finally inhomogeneous, due to the boiling-condensing regime of the coolant. A reactivity initiated ATWS event occurs, where the reactor is becoming critical from time to time, meanwhile the results are demonstrating the strong self-regulating capability of the VVER-440 core also in case when the power rise is starting from low temperature and pressure. In spite of the continuous dilution, in the final phase of the transient the long term average of the power is stabilizing because of the adverse effects of the dilution and the decreasing moderator density.

## Remaining work

There is no remaining work.

## Related publication

*Investigation of boron dilution accidents at POS 5 shut down state, MTA-EK-RAL-2013-746/3-M2, 2014, in Hungarian.*

# DETECTION OF LEAKING FUEL RODS BY NUMERICAL METHODS

*Péter Szabó, Zoltán Hózer*

## Objective

The aim of the calculations was the comparison of three different methods for the detection of leaking fuel rods in a nuclear reactor and the interpretation of the calculated results.

## Methods

Three different numerical methods were applied:

- The RING code was developed at the MTA EK and are in use for the evaluation of on-line measured data at the Paks NPP. It is based on a regression method using iodine and noble gas activities.
- The BME NTI method is regularly applied for the evaluation of fuel campaigns. The method is based on the full activity approach taking into account some standard, reference values.
- The Russian methodology was developed by the fuel supplier. It is based on the experience of leaking fuel operation of several VVER type NPPs. The algorithm of the method was described in a document and it was coded by MTA EK experts.

## Results

Several datasets were used for the comparison. The main conclusions of the first series of calculations are the followings:

- The results of RING and BME NTI calculations were very close to each other for the selected data points. The comparison of the two methods was applied only for some selected datasets that are typical for stabilized conditions.
- The Russian methodology in almost all cases overestimated the number of leaking fuel rods compared to RING results.
- One other difference was found between the RING and Russian methodology results if the tramp uranium on the surface of the core was very small. If the mass of tramp uranium was not negligible, the difference was much less.

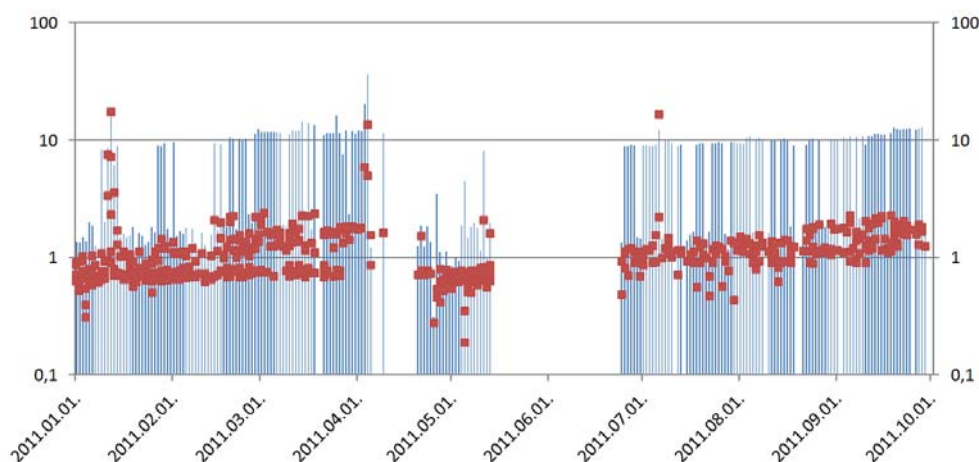


Figure 1: Estimated number of leaking fuel rods in Unit No. 4 of Paks NPP by the Russian methodology (columns) and by the RING code (symbols)

## Remaining work

Systematic comparison will be carried out with a large dataset.

## Related publications

- [1] P. Szabó, Z. Hózer: *Calculations with Russian methodology developed for the detection of leaking fuel rods*, EK-FRL-2014-758-01/01 (in Hungarian)
- [2] P. Szabó, Z. Hózer: *Comparing the Russian methodology and RING code for the detection of leaking fuel rods*, EK-FRL-2014-758-01/02 (in Hungarian)
- [3] Z. Hózer: *Simulation of leaking fuel rods in a VVER reactor*, *Annals of Nuclear Energy*, 70 (2014) pp. 122-129

# ANALYSIS OF CORROSION PARTICLES ORIGINATED FROM THE PRIMARY AND SECONDARY COOLING SYSTEM OF PAKS NPP

*Éva Kovács-Széles, Kornél Fél*

## Objective

Between Centre for Energy Research and PAKS Nuclear Power Plant (NPP) there is a research contract which specifies analysis of corrosion particles originated from the primary and secondary cooling systems of the reactors to detect the origin or source of corrosion. For determination of the nature of these particles (size, morphology, activity, elemental composition, etc.) more, different techniques are used.

## Methods

In this work, more parameters of particle samples originated from the block No. 1 from startup and shutdown period were determined using different analytical techniques: morphology by optical microscopy (OM) and scanning electron microscopy (SEM), activity by gamma-spectrometry,  $^{63}\text{Ni}$  and  $^{55}\text{Fe}$  content by liquid scintillation technique, corrosion products (Fe, Co, Ni, Cr, Zr, Ag) by inductively coupled plasma mass spectrometry (ICP-MS), calculation of the specific activity and the residence time of the particles in the reactor zone, analysis of the filtered particles and also the filtrates.

## Results

During this work several particles originated from the primary and secondary cooling system of PAKS NPP (block No. 1) were investigated. Some pictures taken by SEM can be seen in Fig. 1 and Fig. 2.

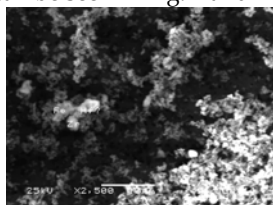


Figure 1: Particles containing also Hf

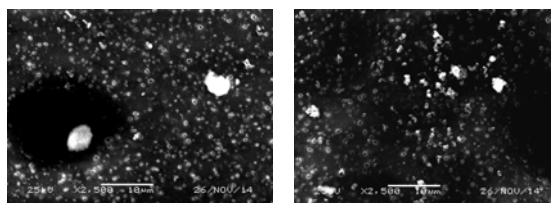


Figure 2: Zr-containing particles

Following the microscopic investigation of the particles it was concluded that the surface coverage of the filters is changing in the starting period. By starting the pumps it is higher (full with iron-oxides containing little Ni and Cr and some Fe-Cr-Ni-oxides) then after the washing and water treatment it decreases. At the starting period significant Zr content was found connecting to the iron-oxides, and Zr-oxides were presented, too. Later the amount of Zr decreased. Still at the starting period Hf was also found in the iron-oxide particles in some cases.

The residence time of the corrosion products in the reactor zone can be calculated from the specific activity of the long-lived  $^{63}\text{Ni}$  isotope (half-life: 100 years). The calculated value of this nuclide was relatively high.

Result of determination of residence time by using the specific activity of the shorter half-life isotopes ( $^{54}\text{Mn}$ ,  $^{55}\text{Fe}$ ,  $^{60}\text{Co}$ ) seems shorter compared to the residence time calculated from the previous method ( $^{63}\text{Ni}$ ). It can be explained that the activation of the particles happened not only during the last campaign but also in earlier once therefore the shorter half-life isotopes have already decayed (assuming the long-term stability of the particles).

## Remaining work

This work was a part of an ongoing research project for PAKS Nuclear Power Plant which will be running until 2016, therefore the analysis of the particles will be continuing in the future.

## Related publications

É. Kovács-Széles: *Korróziós részecskék vizsgálata a primer és szekunder köri hűtőrendszerekben I. and II.*, [in Hungarian] research report for PAKS Zrt., EK-SBL-2013-766-01 (2014)

# REACTOR MATERIALS HANDBOOK

*Attila Kovács, Ferenc Gillemot, Márta Horváth, Ildikó Szenthe,*

## Objective

Long time operation of Nuclear Power Plants (NPP-s) requires time to time the recalculation of the safety of the different equipment considering the ageing of the structural materials, and the more rigorous safety requirements. Different organizations (International Atomic Energy Agency, EU, national regulatory body, ASME (American Society of Mechanical Engineers) etc.) from time to time update their safety related recommendations. The utilities are changing the operational technology, new type of fuels are used, and the ageing of Nuclear Power Plants requires growing amount of repairs and for replacements. All of these activities need the knowledge of the material properties. The properties of the as - produced structural materials may be taken from standards, but the aged properties are only partially found in the different codes. The purpose of this handbook is to collect the existing knowledge on the most important structural materials and to provide them to the designers of the replacement parts, and to the engineers performing new lifetime and safety related calculations. Using a common source of aged material data reduces the discrepancy between the different design and safety calculation groups. Since thousands of different materials are used in an NPP, it is impossible to collect the properties for all of them. The correct description of one type of material takes some month's hard work for highly skilled engineers, but the most relevant materials can be selected and year by year the handbook can be extended.

## Methods

During the first year, the elaboration of the structure of the handbook was the task. Each material will have a general description. This file describes the typical application of the material, summarizes the production technology, provides information on the available forming, welding, machining technologies, and about the replacement qualities. The next file contains the standard and usual chemical compositions. The following group of files contains the mechanical properties of the material in as-received and in aged conditions (thermally aged, radiation damaged, fatigued etc.): yield and ultimate tensile strength, elongation, reduction of area, Charpy impact testing results (sometimes Charpy transition temperature), hardness testing, fracture toughness. The last group of files contain the physical properties of the material important for the designers. Figure 1 shows the draft structure of the handbook.

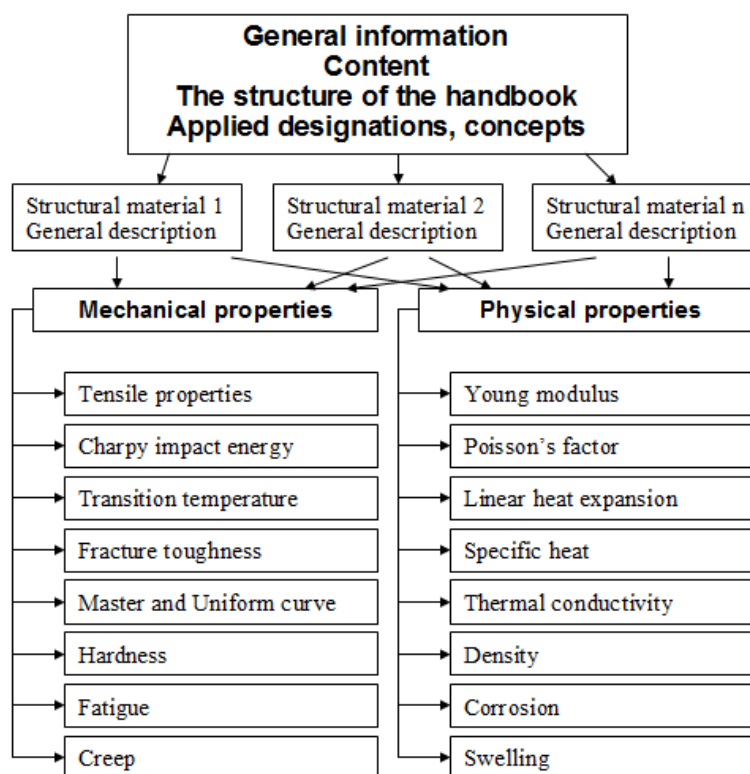


Figure 1: The structure of the handbook

## Results

The structure of the handbook was elaborated in 2014.

## Remaining work

Selection of the materials, collection of the data and filling them into the handbook are the tasks for the following years.

# IMPROVEMENT OF DETERMINISTIC REACTOR PHYSICS CODE SYSTEMS

*Csaba Maráczy, György Hegyi, Emese Temesvári*

## Objective

The accuracy of deterministic reactor physics code systems on higher levels (global and pin-wise level) is greatly affected by the quality of few group constants used in them. Tracking the concentration of  $^{239}\text{Pu}$  on higher levels significantly improved the accuracy of few group constants in case of  $\text{UO}_2$  fuel and light water moderator. The tendency of increasing the fuel discharge burnup in generation 2 reactors and the potential use of MOX (Mixed Oxid) fuel in generation 3 reactors justifies the survey of application of Pu isotopes with higher mass number on these levels.

## Methods

- 2-D deterministic neutron transport calculations with burnup
- Multidimensional approximation of few group cross sections

## Results

The KARATE code system applies the parametrized 2-group cross sections generated by the MULTICELL neutronic transport code. First transport calculations were carried out at wide range parameter combinations. After fitting the coefficients of cross section formulas the database of coefficients was prepared. The evaluation of the cross sections at the necessary parameters is performed during the nodal calculations.

The cross section methodology was tested as follows. Hypothetical fuel history calculations including power density changes and technological parameter variations were carried out in several cases. The reference was the MULTICELL transport code. We have imitated the burnup history calculation with the help of the parametrized cross sections using the PARACELL code. The PARACELL code calculates the same fuel history as the MULTICELL code but uses only the 2-group parametrized cross sections. The PARACELL code has two options:

- Old method: The concentrations of  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Np}$  and  $^{239}\text{Pu}$  are calculated.
- New method: The concentrations of  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{242}\text{Pu}$  are calculated.

The PARACELL code evaluates the effective multiplication factor ( $k_{\text{eff}}$ ) with the parametrized cross sections using the buckling from the MULTICELL criticality calculation. The deviation of  $k_{\text{eff}}$  of PARACELL from one characterizes the accuracy of cross section parametrization. Figure 1 shows the superiority of the new method to the old one, so the explicit calculation of actinides with higher mass number will be applied in the future.

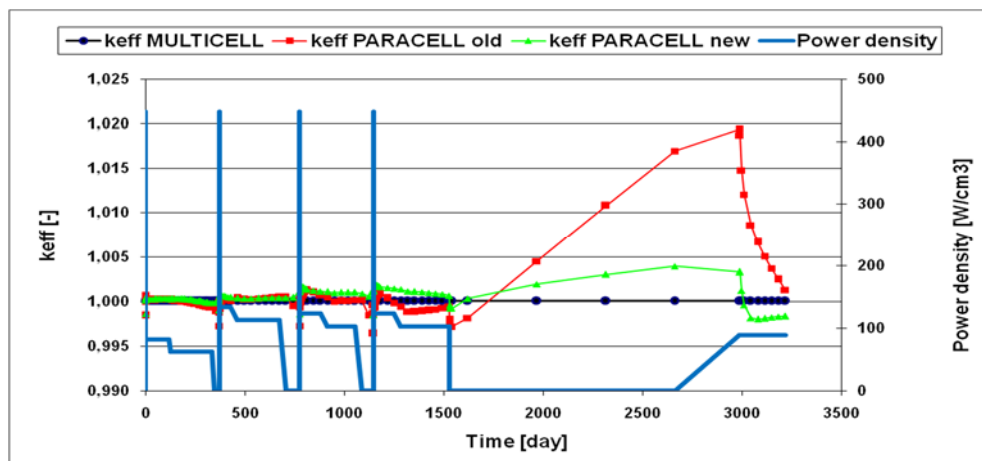


Figure 1: Power history and effective multiplication factor curves for four consecutive cycles, four year cooling and further irradiation in the core

## Remaining work

The work has been completed.

## Related publication

Cs. Maráczy, Gy. Hegyi, E. Temesvári: *Improvement of Deterministic Reactor Physics Code Systems: Parametrization of Few Group Constants with Tracking the Concentrations of High Mass Number Plutonium Isotopes on Higher Computational Levels*, Research Report EK-RAL-2014-785-01-01-M0 (in Hungarian)

# REACTOR NOISE DIAGNOSTICS MEASUREMENTS AT PAKS NPP

*Sándor Kiss, Tamás Czibók, Zoltán Dezső, Károly Krinizs, József Láz, Sándor Lipcsei*

## Objective

Regular reactor noise diagnostics measurements have been performed at Paks NPP since 2000. They were continued also in the present year, and the maintenance of the measurement system PAZAR was also carried out. PAZAR systems are fed by analogous signal sets of the VERONA systems. Main part of our activity is monitoring of the coolant velocity along the fuel bundles equipped with SPND chains, and monitoring of vibration of the core internals.

## Methods

Regular measurements were performed monthly. Long term (1 day to 2 week) measurements were also carried out, usually twice per month. All measurements were taken to the MTA EK for further processing. The assessment of recorded data was performed off-line by means of the evaluation software PAZAR-K. Beyond the statistical evaluation of the regularly measured noise signals, a large subset of the detector signals was continuously monitored for transients.

## Results

Noise data archive was extended with the measurements of the present year.

According to the evaluated data, the average core coolant velocity was quite stable during the year, only usual small fluctuations could be observed at all four reactor units.

The possible vibrations of core internals were also investigated, but no such anomalies were observed in 2014. Reports were compiled for the plant from all measurements.

Files with transient events were collected and classified by events. As an example, the effect of a quick power reduction of approximately 50% on the signals of Unit 4 at Paks NPP is shown in Fig. 1.

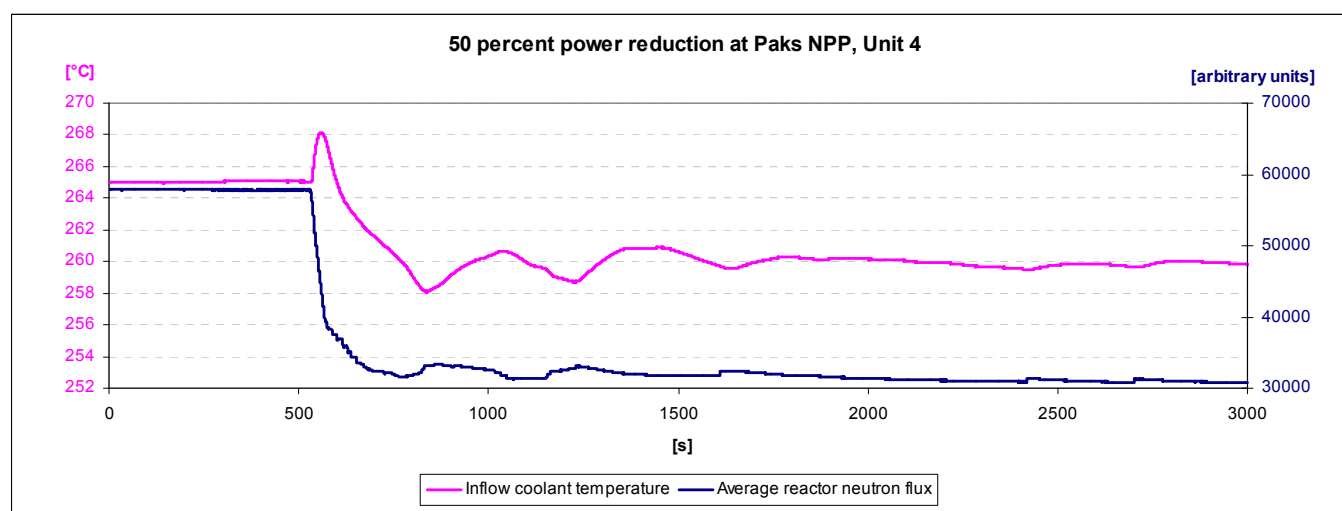


Figure 1: Effect of a quick power reduction at Paks NPP, Unit 4

## Remaining work

Regular noise diagnostic measurements and collection of transient events will be continued in 2015.

## List of abbreviations

MTA EK	Centre for Energy Research, Hungarian Academy of Sciences
NPP	Nuclear Power Plant
PAZAR	Hungarian acronym for Noise Diagnostics System at Paks NPP
PAZAR-K	Signal evaluation software for PAZAR system
SPND	Self Powered Neutron Detector
VERONA	Reactor Core Monitoring System for VVER type NPPs

# INFLUENCE OF THE CROSS SECTION UNCERTAINTIES ON THE MULTIPLICATION FACTOR

*Gábor Hordósy, István Pataki, István Panka*

## Objective

The subcriticality analysis of a spent fuel storage facility is strongly influenced by the uncertainty of the calculated multiplication factor ( $k_{eff}$ ) due to the uncertainties of nuclear cross section data. Traditionally, this uncertainty was determined from comparison of calculated and measured  $k_{eff}$  values for a number of critical experiments. This approach can easily be applied to cases with fresh fuel, because there is a number of publicly available critical experiment with fuel enrichment, moderator, geometry etc. similar to the storage facilities. However, when burnup credit is applied in the subcriticality analysis i.e. the change of reactivity due to the change of composition with burnup is considered, the problem arises that there are no such available critical experiment data where the fuel composition is similar to the composition of the spent fuel. A possible solution is to determine the discussed uncertainty by calculation using the covariance data of the cross sections and use the critical experiments for checking the calculations.

## Methods

Two possible approaches to this problem are known. In the sensitivity/uncertainty method the sensitivities of the multiplication factor to the cross sections are evaluated using the linear perturbation theory. The uncertainty of the multiplication factor can then be determined from the sensitivity matrix and from the covariance matrix of the nuclear data. This method was implemented into the SCALE program package at the Oak Ridge National Laboratory and it is widely used. In the sampling method, energy dependent perturbation factors are generated for cross sections of the relevant reactions. The perturbation factors are generated by random sampling based on the covariance matrices of the investigated cross sections. Performing a number of criticality calculations with perturbed cross section library, the standard deviation of  $k_{eff}$  due to the cross section error can be estimated. This method requires significant computer time but the assumptions of the linear perturbation theory are not used. An additional advantage is that the 95 % / 95 % confidence interval of the calculated multiplication factor can be determined. This method has been implemented using the 44 group covariance matrices distributed by the NEA and the MCNP5 Monte Carlo code.

## Results

The method was tested using 170 low-enriched uranium (LEU) and mixed uranium-plutonium oxide (MOX) critical experiments selected from the International Handbook of Evaluated Criticality Safety Benchmark Experiments. The 95 % / 95 % confidence interval and the standard deviation due to cross section uncertainties of the calculated multiplication factors were determined using the sampling method. The standard deviations were also evaluated by the SCALE code. The standard deviations calculated by the two methods were in good agreement for the LEU experiments, while for the MOX cases the sampling method gave 10-30 percent higher standard deviations. This can be explained by the difference of  $^{239}\text{Pu}$  covariance libraries built into the SCALE code and used in the sampling procedure. The calculated 95 % / 95 % confidence interval includes the measured  $k_{eff}$  values for 168 of the investigated 170 cases. This is a better agreement than what is expected statistically, and it suggests that the covariance data were evaluated by strong conservatism. This agreement is shown in Fig.1 for such MOX cases when the fuel is contained in pins.

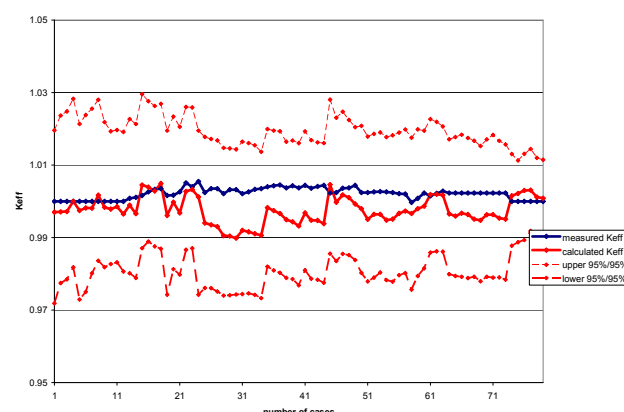


Figure 1: The measured and calculated  $k_{eff}$  values with the 95%/95% confidence interval

## Remaining work

Repeat the calculations with new covariance matrices, investigate the influence of the fission spectrum.



# AGEING OF CONCRETE STRUCTURES AT NPP PAKS

*Tamás Fekete, Tamás Pázmándi, Veronika Bartha<sup>1</sup>, Károly Kovács<sup>1</sup>*

*<sup>1</sup>ÉMI Nonprofit Ltd.*

## Objective

Concrete structures are significant components of nuclear power facilities. They are designed to provide:

- Shielding against nuclear radiation and retaining harmful radioactive material releases;
- Structural support to the mechanical and electrical systems and components; and
- Protection of the systems and components from the environment.

Studies of concrete ageing programs usually use two classifications to group concrete structures. These are: safety significant and environmental exposure. Concrete structures that are classified as safety significant are called Category I concrete structures, according to the NRC (Nuclear Regulatory Commission) terminology. Concrete structures classified as environmental exposure are called Category II.

Category I concrete structures perform one or more of the following safety-related functions:

- Radiation attenuation and shielding;
- Prevention of uncontrolled liquid or airborne radiation releases;
- Structural support for nuclear steam supply system and containment-internal equipment;
- Structural support for redundant safety-related equipment;
- Structural support for heat sink equipment;
- Support for spent fuel pools;
- Protection of safety-related equipment from harmful environment; and
- Separation or "communication" function.

Category I structures are significantly influenced by the nuclear power generation process. Category II concrete structures of a nuclear power plant facility are considered to be conventional structures and are not significantly affected by the nuclear power generation process.

The durability and performance of concrete structures also depend on the severity of the environment in which the structure is located. The concrete structures directly around the reactor pressure vessel experience the majority of irradiation and temperature related degradation during the lifetime of a nuclear power plant (NPP).

As the operation of NPPs extends to several decades beyond the original design lifetime, it is important to ensure that the concrete structure maintains adequate properties also during long term operation, considering that the structural material is subject to damaging effects by neutron irradiation, gamma radiation and higher temperature. As long as the load carrying capacity of the material is required to remain at a sufficiently high level together with its shielding properties, changes in the mechanical properties due to nuclear radiation are of particular significance and may have to be taken into account in future safety analyses.

The goal of the project is to elaborate a database that will contain reliable experimental data for the relevant material parameters of aged structural concretes used at NPP Paks.

## Methods

At first, a literature review has been performed. Based on results of the literature review, a detailed experimental program will be developed. The scope of the experiments is to irradiate different concrete specimens up to different irradiation levels, equivalent to a number of years of operation of the NPP that is beyond the expected lifetime of the plant during long-term operation.

A concept for the test rig and for relevant measurements will be developed. The test rig is planned to contain specimens with diameters up to 4-5 cm. The temperature at the center of the specimens will be held around 100 °C during irradiation.

Temperature, gamma heat, gas and water release, dimensional change measurements are planned during irradiation. Neutron fluence evaluation, remaining activity, volume change, mass change measurements and mechanical tests will be performed after the irradiation.

## Results

The literature review led to the conclusion that the planned experimental program is feasible.

## Remaining work

A detailed experimental program has to be developed, the experimental facilities have to be designed and constructed, and after that the irradiation program has to be implemented. Finally, the material tests have to be performed and the program has to be evaluated.



# NEW VVER FUEL: IMPROVEMENTS, EXPERIMENTAL DATA AND COMPARISON WITH THE MODELS OF THE CODE FUROM

*Katalin Kulacsy, Zoltán Hózer, Emese Slonszki, Péter Szabó, Márton Király, Anna Pintér-Csordás, Eszter Barsy*

## Objective

The steady-state fuel behaviour simulation code FUROM used for normal operation has been developed at MTA EK and its predecessor, AEKI. Further development, verification and validation of the code are constantly on-going tasks: the present work, supported by Paks NPP, is part of this process. On the one hand, the capabilities of the code had to be assessed against the new features of improved VVER fuel types. On the other hand, the models describing the normal operation behaviour of the cladding had to be verified and validated against new or previously not evaluated experimental evidence on both un-irradiated and irradiated cladding specimens.

## Methods

In the first phase of the work, an overview was prepared based on literature, covering the evolution of VVER fuel assemblies (both VVER-440 and VVER-1000) and the resulting changes in fuel characteristics relevant to simulation. Possible needs for code development were identified.

In the second phase, publications and measurements performed at AEKI were used to make a compilation of data specific to cladding behaviour.

In the third phase, calculations were made using the models implemented in the code FUROM and the results were compared to the data mentioned above.

## Results

New fuel designs include changes

- in structure and/or geometry and
- in the composition and/or texture of components,

with the purpose of increasing safety and allowing higher burn-up and longer dwelling time in the reactor. Assembly geometry is not modelled in the code FUROM, only the geometries of the pellet and of the cladding are therefore relevant. Major changes in the geometry of the pellet, new gadolinia contents, erbium doping and burn-up values beyond the validity of the current models may necessitate new radial profiles fitted to neutron physics calculations or the implementation of a neutron physics module into the code. Large-grain fuel changes the fission gas release kinetics, therefore the models need to be evaluated against experimental data. Pellet dishing is currently not modelled but may be necessary in the future.

As regards cladding mechanical properties, the available data covered Young's modulus, Poisson's ratio, yield strength, irradiation growth, ultimate tensile strength, ultimate elongation and creep, and additional data could be found on thermal properties (thermal expansion and thermal conductivity). Since cladding failure is not modelled in normal operation conditions, ultimate tensile strength and ultimate elongation are not relevant to the validation of the code FUROM.

Although models for Young's modulus and Poisson's ratio include neither anisotropy nor the effect of irradiation, both of them agree well with experimental data on un-irradiated and on irradiated samples. Yield strength is also accurately modelled, especially at operating temperatures. Irradiation growth is of particular interest, as the improved Russian alloy E110G exhibits much smaller growth than the original E110. The irradiation growth calculated by the code gives acceptable results for E110 as well, but it is closer to the behaviour of E110G. Cladding creep is overestimated by the code. Finally, both thermal expansion and thermal conductivity are accurately modelled.

## Remaining work

The review has been completed, creep model development is underway.

## Related publications

- [1] E. Slonszki, P. Szabó, K. Kulacsy, Z. Hózer: *Directions of improvement for VVER fuel*, EK-FRL-2014-961-01/01 (2014), in Hungarian
- [2] M. Király, A. Pintér-Csordás: *Compilation of VVER cladding mechanical properties in normal operation*, EK-FRL-2014-961-01/02 (2014), in Hungarian
- [3] K. Kulacsy, E. Barsy: *Comparison of VVER cladding mechanical properties in normal operation to the models implemented in the code FUROM*, EK-FRL-2014-961-01/03 (2014), in Hungarian

# PARTICIPATION IN THE OECD SCIP PROJECT

*Emese Slonszki, Zoltán Hózer*

## Objective

The overriding objective of SCIP and SCIP II has been to contribute to establishing of more reliable fuel, by further deepening the understanding of mechanisms leading to fuel failures driven by pellet-cladding mechanical interaction. Although a lot of valuable data has been acquired so far, the basic mechanism of PCI failures is still not thoroughly understood. Thus, it is obvious that at least part of the efforts within SCIP III will be dedicated to the same valuable objective. Issues to be addressed include the impact of different ramp rates on PCI performance and effects taking place at the pellet-cladding interface.

## Methods

The fuel rod cladding fulfils an important barrier function during normal reactor operation and anticipated operational occurrences. It prevents fission products and actinides from being released into the reactor coolant. Under design basis accident conditions like loss-of-coolant (LOCA) and reactivity initiated accidents (RIA), the cladding is important also for maintaining a coolable geometry and for ensuring safe shutdown and subcriticality of the reactor core. Although fuel rod failure rates have decreased considerably, the significance of a single failure and of its consequential costs is much higher in today's competitive environment. On the other hand, unnecessary operational limitations, maintained in order to reduce the risk of potential fuel rod failures, should be eliminated in order to reduce fuel cycle costs. This is only possible, if failure mechanisms are understood and can be modelled quantitatively.

The present work provides an overview of results of the first two parts of the SCIP project, SCIP and SCIP II and the aims of the third part, SCIP III [1].

## Results

The Studsvik Cladding Integrity Project, SCIP, was launched in 2004. It was a 5 years OECD/NEA Joint Project operated by Studsvik with about 30 participating organisations, including regulatory bodies, research institutions, utilities and fuel suppliers from 13 different countries. SCIP aimed at studying basic phenomena of fuel rod failures driven by pellet-cladding mechanical interaction, thus contributing to a better understanding of fundamental failure mechanisms. Pellet-cladding mechanical interaction, primarily as a function of burnup, was studied in a number of ramp tests. Key parameters important for hydrogen-induced failures, in particular delayed hydride cracking and failures due to embrittlement of the cladding as a consequence of hydriding, are now much better understood thanks to SCIP and could in many cases be quantified. In the case of failures caused by stress corrosion cracking from the inside of the fuel rod ("classical" pellet-cladding interaction, PCI), equipment simulating in-core conditions was significantly improved. From the very beginning, SCIP prioritised studies on cladding. Studies on pellet-related parameters were in general not considered, primarily due to limited resources and funding. Early in SCIP already, it became obvious that pellet properties, dramatically changing with burnup, need to be considered as well in an integral description of PCI/PCMI. Consequently, the 5-year continuation of SCIP, SCIP II, aims at improving the knowledge on the role of the fuel pellet related to fuel failures driven by pellet-cladding mechanical interaction (PCMI). The four Tasks of SCIP II deal with a review of old ramp test results, with pellet-cladding mechanical interaction, with chemically assisted stress corrosion cracking (pellet-cladding interaction, PCI) and, as a carry-over and continuation of work performed in SCIP, with hydrogen-induced failures. Performance of advanced fuel types with additives and large grains is assessed by means of the most advanced available examination techniques in comparison with standard fuel. The focus of SCIP III will be on LOCA issues, in particular on fuel fragmentation, relocation and release, on the influence of microstructural effects and of transient fission gas release on LOCA performance, on the influence of axial constraints, and on oxidation and post-quench ductility. The consequences of cladding overheating at lower than LOCA-typical temperatures and for shorter periods of time will be addressed as well. In a second task, PCMI and PCI issues will be further studied, amongst others the beneficial effect of slow and staircase ramp tests compared with fast ramps leading to PCI failure. Finally, modelling in SCIP III shall be an integrated part of the project and shall be planned and managed by Studsvik.

## Remaining work

The MTA EK evaluates the results of the project activities in the research report annually.

## Related publication

E. Slonszki, Z. Hózer: *Summary on SCIP SCIP II results and SCIP III plans*, EK-FRL-2014-962-01/01 (in Hungarian)

# PREPARATION OF THE CODEX-LOCA EXPERIMENTS

*Imre Nagy, András Vimi, Mihály Kunstár, Zoltán Hózer*

## Objective

High temperature experiments will be carried out in the CODEX facility to simulate LOCA behavior of E110G cladding. The CODEX facility has to be rebuilt for the tests. In the first phase of the project the main objectives were the completion of technical design and the construction of the main components.

## Methods

In the new design of the CODEX facility the experience from the previously executed tests was taken into account and some special new solutions were applied to fulfill the special requirements of the LOCA test.

## Results

The fuel rod design was a key question in the preparation of the experiment, since the internal heating and pressurization of the individual fuel rods had to be performed parallel during the experiments.  $\text{Al}_2\text{O}_3$  pellets with double hole are applied in the new design. The top of the fuel rods are closed by Zr plugs and electrical connections are placed only to the bottom of the rods. The pressurization can be done with argon gas through special connections to each rod.

The testing of steam generator and superheater units were successfully completed up to 200 °C. New condenser unit was purchased and connected to the test section.

The gas composition measurements will be carried out by the quadrupole mass spectrometer, which is connected to the exit of test section. The mass spectrometer was tested separately. Additional thermal conductivity measurement detector will be used to measure hydrogen content in the coolant. The calibration of the detector was completed.

New data acquisition system (supplied by National Instruments) will be used in the LOCA tests.

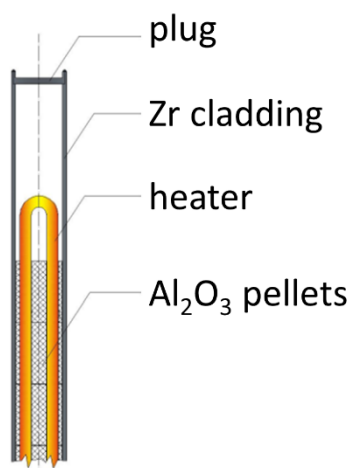


Figure 1: Scheme of rod heating (left), 7 rod bundle (center) and mass spectrometer

## Remaining work

It is intended to carry out several LOCA tests in the new CODEX facility.

## Related publications

- [1] I. Nagy, A. Vimi, M. Kunstár, Z. Hózer: *Preparation of high temperature experiments for the simulation of E110G cladding under LOCA conditions*, EK-FRL-2014-963-01/01 (in Hungarian)
- [2] I. Nagy, A. Vimi, M. Kunstár, Z. Hózer: *High temperature integral facility for the simulation of E110G cladding under LOCA conditions*, EK-FRL-2014-963-01/02 (in Hungarian)
- [3] A. Vimi, Z. Hózer, I. Nagy, M. Kunstár: *New experimental investigations on the CODEX facility*, 20th International QUENCH Workshop, Karlsruhe, November 2014.

# EVALUATION OF FRACTURE TESTS USING ADVANCED MODELS

*Tamás Fekete, Dániel Antók, Levente Tatár*

## Objective

The Reactor Pressure Vessels (RPVs) are the lifetime limiting components of a Nuclear Power Plant (NPP) and irradiation embrittlement is the leading ageing mechanism of them. Evaluation of safety and structural integrity of long term operating RPVs requires thorough knowledge on fracture mechanics properties of their structural materials in aged state. Knowledge of them properties depends on the evaluation methodology of the material tests. The original surveillance program produced fracture mechanical tests that served as database for lifetime extension, but it has to be complemented by further measurement results in order to cover newer aspects of material characterisation required for later phases of the Long Term Operation (LTO). The main reason of the claim for new measurements is the rapid development of the theory and numerical methods used for structural integrity calculations of RPVs. Structural integrity calculations are tools to evaluate the safety of flawed or damaged structures. Today, 3D RPV models are commonly used during Pressurised Thermal Shock (PTS) structural integrity calculations. PTS phenomenon can occur when in some accidental situations extra quantity of cooling water flows into the RPV, causing severe overcooling of the vessel wall. A PTS event can cause a dangerous situation regarding the structural integrity of an RPV, as high thermal gradient develops through the vessel wall, causing high thermal stresses, which are superposed to stresses originating from internal pressure. The main goal of PTS calculations is to assess allowable service time of the RPVs from PTS point of view. Today, there is a chance to bring in more advanced theoretical and numerical methods into PTS calculation methodology. But even nowadays the evaluation of fracture tests according to current standards are based on simplified theoretical models and numerical procedures. The use of different models within structural integrity calculations and within the evaluation of material tests is incorrect on a theoretical level. Furthermore, it can lead to inaccurate results regarding allowable service time of the RPV.

The goal of the project is to develop and verify an advanced evaluation methodology of fracture tests, using the same theoretical models of continuum mechanics/thermodynamics and numerical methods which will be used for PTS structural integrity calculations in the future.

## Methods

The methodology of calculations has been developed at MTA EK, applying the theory of material or configurational forces to fracture mechanics. The theory of configurational forces is a unified theory of nonlinear continuum mechanics and rational – nonequilibrium– thermodynamics with internal variables. According to the theory of configurational forces, the driving force on a crack tip can be described by the (generalized)  $J$ -integral in case of elastic-plastic, materially inhomogeneous materials, independently from scale of deformation, so the theory can be used for solving problems with large deformations. A 3D finite element model has been developed for the specimen geometry (Figure 1). Large deformation plasticity theory is applied to model effects of geometrical and material nonlinearities that are present in the system during calculations. Flow curves of structural materials were developed from tensile test results. Numerical calculations were performed by using the Msc.MARC FEM code.

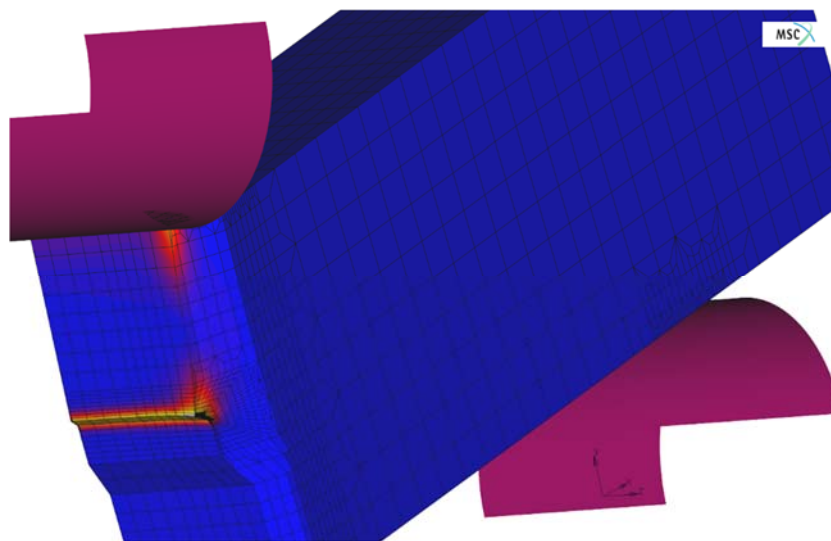


Figure 1: FEM model of a 3 point bend fracture specimen showing equivalent plastic strain field during loading

## Results

3D finite element models of the 3 point bend fracture specimens have been developed and tested.

## Remaining work

The experimental program has to be performed and evaluated using the newly developed models.

# SIMULATION OF TELESCOPE SIPPING TESTS WITH LEAKING FUEL ASSEMBLIES

*Zoltán Hózer, Katalin Kulacsy*

## Objective

The TSKGO computer code was developed for the simulation of leaking fuel rods after their removal from the reactor, including the testing telescope sipping (TS) equipment. In 2014, the main objectives of the further development were addition of  $^{134}\text{Cs}$  to the list of simulated isotopes and the investigation of correlation between different leaking fuel parameters.

A new module of the TSKGO program simulates the primary coolant activity concentrations, the background activity in the refuelling pit and calculates the corresponding TS signal.

## Methods

The inclusion of the  $^{134}\text{Cs}$  into the list of isotopes needed modification of the FUROM code that provides input data for the TSKGO simulation and extension of the decay process simulation in the TSKGO program. The new models describe the formation of  $^{134}\text{Cs}$  isotope from  $^{133}\text{Cs}$  by neutron capture. The gap activity calculations are based on the detailed simulation of diffusion process.

## Results

The results of calculations provided detailed information on the effect of defect size, defect location, burnup and time of leaking fuel operation in the reactor.

The calculations demonstrated that the activity release from leaking fuel rods is a complex phenomenon influenced by several effects. For this reason, the TS signal is also affected by many different conditions and the correlations between TS signals and other parameters needed detailed modelling of many phenomena. The defect location and the internal gas volume in the fuel rods seem to be important factors in the TS testing.

According to the calculated results, even those leaking fuel rods can produce large TS signal which showed only moderate activity release in the reactor.

The background activities in the primary water (originated from leaking fuel rods during shutdown spiking) are low compared to the activity of water samples taken during TS testing.

- The TS signals from noble gases are at least two orders of magnitude higher than the background signal.
- The iodine and cesium activity concentrations in the samples taken during TS testing are at least one order of magnitude higher than the activity concentration in the refuelling pit.

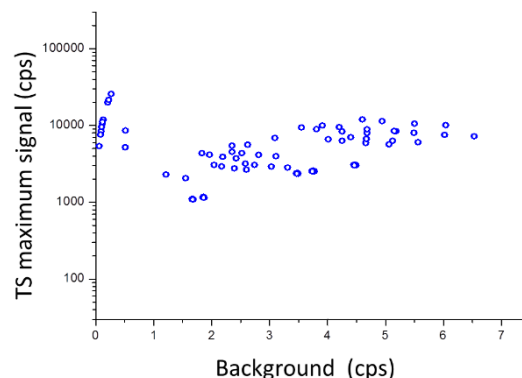


Figure 1: Calculated TS maximum signal as function of background

## Remaining work

The TSKGO code will be applied for the simulation of a fuel assembly identified at the Paks NPP.

## Related publications

- [1] K. Kulacsy, Z. Hózer:  $^{134}\text{Cs}$  model development for the TSKGO code, EK-FRL-2014-761-01/01 (in Hungarian)
- [2] Z. Hózer: Correlation between normal operational activity, iodine spiking peak and telescope sipping signal, EK-FRL-2014-761-01/01 (in Hungarian)

# POST IRRADIATION EXAMINATION OF E110 AND E110G ZIRCONIUM FUEL CLAD

*Attila Kovács, Ferenc Gillemot, Ildikó Szenthe, Márta Horváth*

## Objective

In Nuclear Power Plants (NPP) three barriers are between the public and radioactive fuel materials: the fuel clad, the pressure vessel and the containment system. These are highly safety related parts of the NPP-s. The leaking of the fuel pollutes the primary circuit and the leaking rods have to be removed from the reactor core. The unplanned temporary shut down of a unit causes high loss for the NPP, consequently the knowledge of the service ageing of the different zirconium fuel clad materials is important for the safe and economical plant operation. During normal operation, the main ageing mechanism is the radiation embrittlement. The high energy neutron irradiation in the core changes the mechanical properties of the zirconium alloys. Stable and un-stable matrix damage (mainly due to the increase of the number of lattice defects) occurs during service in the material increasing the hardness and decreasing the ductility. During operational temperature the diffusion partially eliminates the ageing. The purpose of the project is to compare the ageing of the E110 and modified E110G type fuel clad materials and to collect new information on the radiation ageing effect and recovery of these materials.

## Methods

Research reactor irradiation will be used for systematic study of the embrittlement rate. Samples of both type of zirconium alloys will be irradiated at the Budapest Research Reactor with two different fluences. For this purpose new irradiation rig has been prepared and research plan has been elaborated. At operational temperature, radiation embrittlement and diffusion recovery of the zirconium alloys exists at the same time, consequently the degradation will be saturated above certain fluence level. To collect new information for evaluation on the saturation level of the studied different alloys the samples are planned to be irradiated in two different fluxes using different levels of the irradiation rig. After irradiation the mechanical properties will be measured and compared with the properties of the as-received materials. Some already irradiated zirconium pipe are already included into the testing program.

The fuel clads are small diameter (8-10 mm) and small wall thickness (less than 1 mm) pipes. Standard tensile samples can't be produced from them. Technology and equipment have been elaborated to produce 2 mm wide rings (see in Figure 1) and 8 mm long pipes for testing. Since the small size of the samples, exact geometry has to be machined to ensure the acceptable scatter at testing. Devices and technology for room and elevated temperature tensile and compression test of these nonstandard irradiated samples also had to be developed.

To study the recovery of the irradiation embrittlement, different heat treatments in neutral gas atmosphere are used to avoid surface oxidation. The heat treatments are performed at operational temperature range up to 720 hours. To simulate the long term operation effect, elevated temperature (500 °C) accelerated tests using the Arrhenius law are also in the research plan.

## Results

The three years study started in 2014. The testing program has been elaborated, irradiation rig has been partially produced. The testing technology of irradiated samples also has been developed and testing equipment are prepared. A series of heat treatments on the previously irradiated samples have also been made.

## Remaining work

New specimen production, further irradiations and heat treatments are planned for 2015, and most of the testing and evaluation of the results, preparation of the final report will be performed during 2016.



Figure 1: The dimensions of tensile rings

# SECONDARY DEFECTS OF NUCLEAR FUELS

*Emese Slonszki, Zoltán Hózer*

## Objective

In the presence of the “initial defect” the term “secondary damage” (“secondary defect”) means defects generated under the effect of coolant penetrated into the fuel rod through the initial defect. These defects are as follows: fragile breakaway of plugs, visually registered through-cracks and hydride spots spreading on the outer surface of cladding.

## Methods

Massive hydriding of zirconium cladding in defective LWR (Light water reactor) fuel rods may lead to severe secondary failures. Formation of secondary defects results in increased activity release into the coolant and has even caused early shutdown of some plants.

The present work gives review types of the secondary failures and the phenomena which are responsible for the formation of them in particular VVER fuels. Phenomenology of secondary hydriding is well known. Once a primary defect in cladding is formed, water enters the fuel rod and flashes into steam. Steam oxidation of both fuel and inner cladding surface can generate enough hydrogen to break down the protective properties of  $ZrO_2$  and to cause excessive hydrogen pick-up. It is commonly accepted that “enough” hydrogen means oxygen-starved conditions when hydrogen content in gas mixture is substantially higher than that of steam.

The different types of secondary damages affecting failed rods are classified in the following way: “sunburst”, “blister” or “bulges”, perforation or holes and small cracks. Deterioration of a fuel rod beyond these stages can lead to two specific forms of severe degradation. One form is long axial cracks or “splits” (fuel crack is between 15 cm and 3 m) and a second form of degradation is the circumferential break, in which cladding is massively hydrided around enough of the circumference to literally break into two sections.

A number of mechanisms have been proposed to explain axial splitting: embrittlement of the cladding, fracture toughness, delayed hydride cracking, corrosion hydrogen cracking, hydrogen assisted localized shear, crack velocity and source of stress.

## Results

The main mechanism responsible for the majority of cases of the VVER fuel rod perforation is debris-damage of the claddings. Debris-fretting of the claddings spread randomly over the fuel assembly cross-section and they are registered in the area of the bundle supporting grid or under the lower spacer grids along the fuel assembly height. In the WWER (water water energy reactor) fuel rods, the areas of secondary hydrogenizing of cladding are spaced from the primary defects by  $\approx 2500$ -3000 mm, as a rule, and are often adjacent closely to the upper welded joints. There is no pronounced dependence of the distance between the primary and secondary cladding defects neither on the linear power, at which the fuel rods were operated, nor on the period of their operation in the leaky state. The time period of the significant secondary damage formation is about  $250 \pm 50$  calendar days for the VVER fuel rods with slight through primary defects ( $\approx 0.1$ -0.5 mm<sup>2</sup>) operated in the linear power range 170-215 W/cm. Cladding degradation taking place due to the secondary hydrogenising does not occur in case of large through debris-defects during operation up to 600 calendar days.

## Remaining work

In the second part of this work (2015) we will develop the TSKGO program. This computer program will be able to simulate the secondary failures.

## Related publication

E. Slonszki, Z. Hózer: *Secondary failure of NPP fuel rods*, EK-FRL-2014-966-01/01 (in Hungarian)



# TRANSPORT OF LEAKING FUEL ASSEMBLIES TO THE INTERIM DRY STORAGE FACILITY

*Zoltán Hózer, Péter Szabó*

## Objective

The main objective of the present work was the development of a procedure for the Paks NPP on the transport of leaking fuel assemblies to the interim dry storage facility.

## Methods

During the development of the proposed procedure, the existing examination and calculation methods and the technical possibilities of the Paks NPP were taken into account.

## Results

The proposed procedure consists of eleven main steps:

- 1) Evaluation of primary coolant activity concentrations.** The RING code and another domestic procedure can be used for the evaluation of iodine and noble gas activities. On the basis of analyses decision can be made on the necessity of sipping test.
- 2) Estimation of the number of leaking fuel rods in the reactor core.** The RING code and two other calculational methods can provide estimation on the number of leaking fuel rods in the core. If the three methods give different results, the maximum value should be taken into account.
- 3) Burnup estimation of the leaking rods.** The ratio of measured  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  activities can be used for burnup estimation.
- 4) Analyses of power variation transients.** If the normal operational parameters indicate the presence of leakers, the activity concentrations during transient should be checked. The temporary increase of fission product concentrations in the water would be another sign for the presence of the leakers. The peak activities cannot be directly correlated with the number of leakers.
- 5) Analyses of shutdown transient.** Iodine and noble gas activity concentrations must be checked for the shutdown period. It is expected that maximum iodine spike takes place during shutdown. The iodine spiking is a direct sign for the presence of leakers, but the peak activities cannot be directly correlated with the number of leaking rods.
- 6) Sipping during refueling or in the spent fuel pool.** Sipping of outloaded fuel assemblies should be carried out if the normal operational or shutdown data indicated leakers in the core. Using the sipping technique, the leaking assemblies can be identified. Even if the signal of the sipping detector is weak, but it is suspected that the assembly contains leaking rods, the assembly should be handled as a leaker.
- 7) Estimation of the number of leaking fuel rods in the identified assembly.** The number of leaking fuel rods in the core and the number of identified leaking fuel assemblies can serve as conservative approach to estimate the number of leaking rods in the given assembly.
- 8) Analyses of  $\text{UO}_2$  release.** Visual examination and coolant U concentration measurements can indicate that fuel fragments can be released from the fuel rod. The leaking assembly with the possibility of  $\text{UO}_2$  fall-out will be stored in special cask in the spent fuel storage pool. If there are no signs of  $\text{UO}_2$  fall-out, the identified leaker assembly can be stored together with the intact assemblies in the spent fuel pool.
- 9) Activity measurements in the spent fuel pool water.** If leaking fuel assemblies are stored in the spent fuel storage pool, the trends of activity concentrations must be regularly evaluated. The release rate from leaking rods can be well evaluated from the periods without the operation of water purification system.
- 10) Sipping in the spent fuel pool.** Before the transport of leaking assembly to the dry storage facility an additional sipping test is suggested.
- 11) Measurements during transport to dry storage facility.** The activity release must be followed in the transport container and in the handling equipment at the dry storage facility.

## Remaining work

The applicability of the proposed procedure will be demonstrated with real data of a leaking fuel assembly from the Paks NPP.

## Related publication

Z. Hózer, P. Szabó: *Procedure for the transport of leaking fuel assemblies to the interim dry storage facility*, EK-FRL-2014-964-01/01 (in Hungarian)



## **II. GENERATION IV. REACTORS**

# EXPERIMENTAL RESULTS ON IRRADIATED SAMPLES IN THE FRAMEWORK OF MATTER PROJECT

*Attila Kovács, Levente Tatár,  
Ferenc Gillemot*

## Objective

As a prerequisite for standardization of materials used in future Generation IV reactors, the MATTER (MaTerial TEsting and Rules) project focuses on the research for candidate materials for these reactor types. Special attention is paid to P91 and 316LN type steels. 316L is a stainless steel, widely used in industry, with well-known properties. 316LN is a variant of the 316L steel, which satisfies the more severe requirements of the nuclear industry with more strict limits on impurities.

Our knowledge is more-or-less limited on the properties of these steels in the conditions of high temperature irradiations which correspond to the conditions that will probably be present in Generation IV reactors. The objective of this work was to obtain experimental results on the tensile and fracture properties of 316LN steels after high temperature irradiations at different temperatures.

## Methods

The first step in the preparation of the experimental work was an activity calculation to assure that by the end of the project the specimens would not be too active to be handled during the experiments. In the 316LN steel the content of Ni and Cr is high. Thus due to irradiation radioactive elements with high activity and long decay are produced. The need to finish the mechanical tests in the framework of the MATTER project, the estimated activation of samples and the dose limit ( $4\mu\text{Sv}$ ) for our lab limited the total irradiation time to 3 reactor cycles (campaigns).

From our project partners we have received a 316 LN plate containing weldment with gross dimensions of  $400 \times 200 \times 15 \text{ mm}^2$ . Full-size V-notched Charpy and miniature tensile specimens were cut from the plate, some of them containing only base metal and some of them containing weldment.

The irradiations were done in the Bagira3 irradiation rig which, unlike previous Bagira1 and Bagira2 rigs, can withstand much higher temperatures as the target holder is made of titanium alloy. Irradiation temperatures can be controlled between  $150\text{--}650^\circ\text{C}$  with gamma and electric heating and helium-nitrogen gas mix cooling. To fine-tune the temperatures, the electric heating is divided into six separately controlled zones, each of them having its own thermocouple and heating element. The rig has a detachable specimen holder, unique for each irradiation. The specimen holder used for the present irradiation is shown in Figure 1. The zone which corresponds to the miniature tensile specimens is clearly distinguishable.

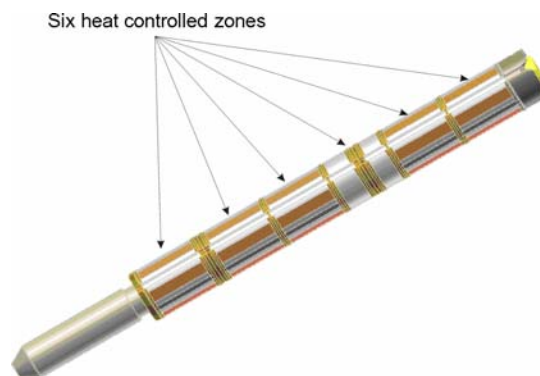


Figure 1: Specimen holder

Temperatures were recorded during the irradiation. Figure 2. shows the recorded temperatures during irradiation for the irradiation campaign no. 2. Time is presented in kiloseconds as it is a suitable unit for irradiation campaigns.

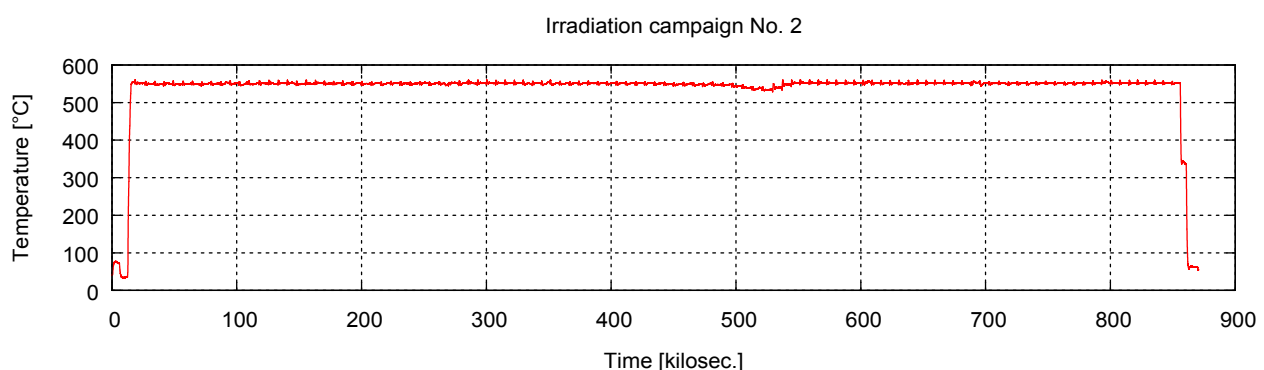


Figure 2: Temperature evolution during the second irradiation campaign

## Results

For the two materials (316LN and 316LN weldment) Vickers-type hardness measurements, Charpy impact and tensile tests were performed in both irradiated and initial state. Tensile tests were done at room temperature and at 550 °C. Fracture surfaces were examined too.

Table 1. shows the hardness before and after irradiations for both materials.

Table 1: Hardness measurement results (average of individual measurements)

	Base metal	Weldment
<b>Before irradiation</b>	300 HV	343 HV
<b>After irradiation</b>	256 HV	522 HV

Standard V-notch Charpy measurements had been performed according to the ASTM requirements. Instrumented Charpy hammer has been used, loads and displacements were recorded. Typical force-displacement curves are presented in Fig. 3.

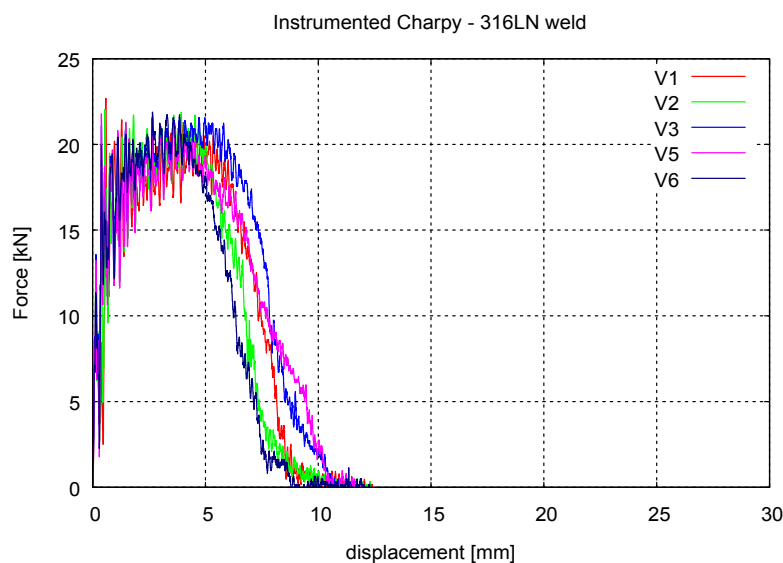


Figure 3: Typical force-displacement curves during Charpy impact test for irradiated weld metal

Figure 4. presents the variation of the ultimate tensile strength for unirradiated and irradiated base metal and weld.

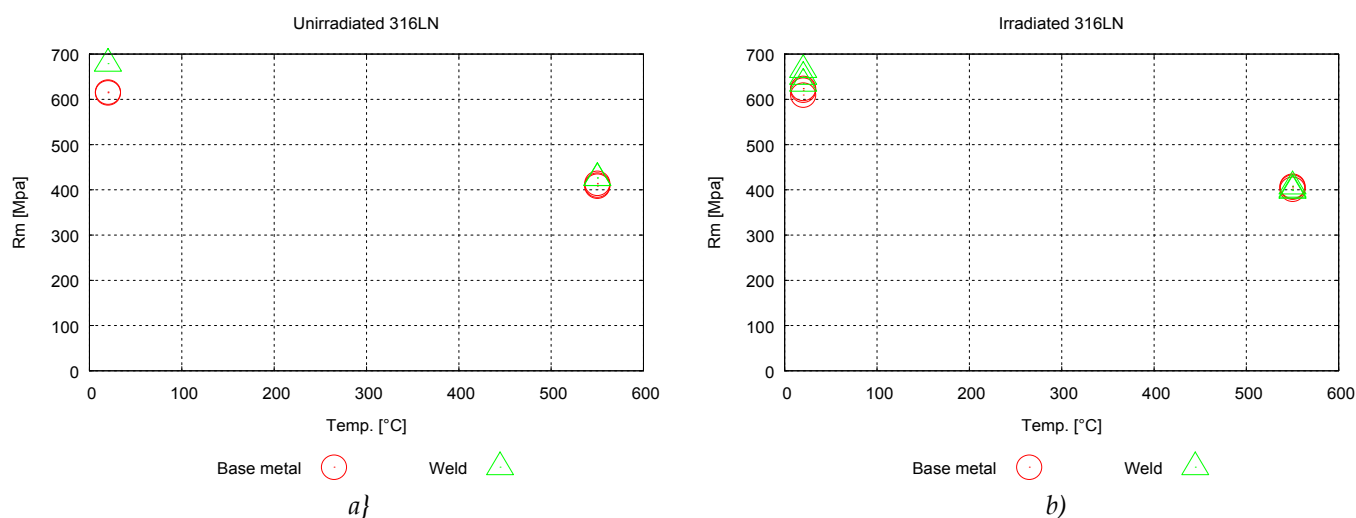


Figure 4: Ultimate tensile strength vs. temperature for unirradiated a) and irradiated b) 316LN base metal and weld

In conclusion, with the currently obtained radiation damage at high temperature (550°C, approx. 0.05 dpa) both 316LN base metal and its weld remain in ductile state, with only very slight changes in ductility. There is a small decrease of the hardness for the base metal (14%) and a more significant increase (34%) for the weld material. Examination of the fracture surfaces shows a clear distinction between the base metal and the weldment, but no clear distinction between irradiated and unirradiated samples.

# SUPERCritical WATER REACTOR – FUEL QUALIFICATION TEST

Csaba Maráczy, György Hegyi, István Trosztel

## Objective

The aim of the SCWR-FQT (Supercritical Water Reactor - Fuel Qualification Test) Euratom-China parallel project is to design an experimental facility for qualification of fuel for the supercritical water cooled reactor. The facility is intended to be operated in the LVR-15 research reactor in the Czech Republic. This reactor enables to replace one of its assemblies with a pressure tube containing a four rod fuel bundle, which shall be connected with coolant pumps, safety and auxiliary systems to simulate a supercritical water environment. All necessary documents required for licensing of the FQT facility by the Czech regulator shall be the outcome of this project. The Centre for Energy Research participated in the 3D steady state and transient analysis of LVR-15 with the fuelled loop. The Reactivity Initiated Accident (RIA) analysis was carried out with the KIKO3D-ATHLET coupled neutronic-thermohydraulic dynamic code.

## Methods

- 3-D dynamic coupled neutronic-thermohydraulic calculations of LVR-15 with the FQT facility.

## Results

With KIKO3D-ATHLET the conservative analysis of the RIA events of the LVR-15 affecting the test section fuel bundle were carried out. The conservative approach for the dynamic calculations means the use of worst case bounding parameters, e.g. reactivity coefficients, control rod worth etc.

In case of the inadvertent control rod withdrawal with scram (Anticipated Operational Occurrence) the 120% power limit for scram in LVR-15 limits the power of FQT fuel rods. As the test section is operated at coolant temperatures below the pseudo-critical point, the coolant temperature rise is minimal during the rod withdrawal, the clad and fuel centerline temperatures are far from AOO limits of 850 °C for clad and melting temperature for UO<sub>2</sub>. The pressure rise is mild during the transient.

In case of the inadvertent control rod withdrawal without scram, the pressure relief valve effectively controls the pressure increase in the FQT loop, according to the parametric studies. However, the fuel integrity is jeopardized by the fuel centerline temperature. To avoid FQT fuel melting during ATWS transients, LVR-15 operator intervention times were calculated for a number of inserted reactivity values. The pressure in the cold leg (CL), in the core outlet and in the pressurizer (PRZ) of the FQT loop can be seen in Figure 1 during the periodic actuation of the pressure relief valve.

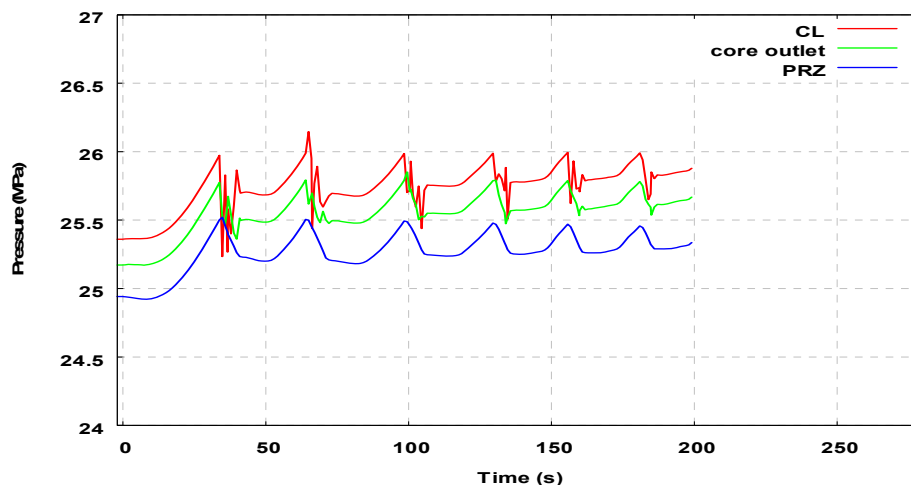


Figure 1: Coolant pressures in the FQT primary loop.

## Remaining work

The work has been completed.

## Related publications

- [1] M. Ruzickova, T. Schulenberg, D. C. Visser, R. Novotny, A. Kiss, Cs. Maráczy, A. Toivonen: *Overview and Progress in the European Project: „Supercritical Water Reactor – Fuel Qualification Test“*, Progress in Nuclear Energy, 77, 2014
- [2] Cs. Maráczy, Gy. Hegyi, I. Trosztel, G. Hordósy, Á. Brolly: *RIA Analysis of the SCWR-FQT Facility in the LVR-15 Research Reactor*, The 19<sup>th</sup> Pacific Basin Nuclear Conference (PBNC 2014), Vancouver, British Columbia, Canada, 24-28 August, 2014, Paper: PBNC2014-045, ISBN:978-1-926773-16-2
- [3] M. Ruzickova, T. Schulenberg, D. Visser, Cs. Maráczy, A. Toivonen, A. Kiss, R. Novotny: *Overview and Progress in the European Project: „Supercritical Water Reactor – Fuel Qualification Test“*, The 19<sup>th</sup> Pacific Basin Nuclear Conference (PBNC 2014), Vancouver, British Columbia, Canada, 24-28 August, 2014, Paper: PBNC2014-107, ISBN:978-1-926773-16-2

# PARTICIPATION IN THE ESNII PLUS EU PROJECT

*Zoltán Hózer, János Gadó, András Keresztúri, Emese Temesvári, Nóra Vér*

## Objective

The ESNII Plus project (2013-2017) merges the contribution of 35 European partners in order to support the development of a federating body to ensure efficient EU coordinated research on Reactor Safety for the next generation of nuclear installations.

## Methods

The experts of MTA EK participate in several work packages of the ESNII Plus project. The activities in 2014 were characterized by literature review and technical specification activities. The main emphasis in the work laid on MTA EK is of gas cooled fast reactors GFR and ALLEGRO. The main topics of our contributions are the followings:

- Structuring ESNII for HORIZON 2020
- Strategic roadmapping
- Support to facilities development
- Industrial perspectives
- Training and dissemination
- Core Safety
- Fuel Safety
- Instrumentation for safety

## Results

MTA EK co-ordinates the work package on “Support to facilities development”. The first meeting on these work packages was held in Budapest, in November 2014. The participating organizations reviewed their potential contribution to “Identification of functional specifications of the R&D facilities” and “Qualification and testing infrastructure for irradiation programme”. It was agreed that a special meeting will be organised for “Siting and project licensing for advanced fission demonstrators” activities in 2015.

The ALLEGRO core specifications were produced. The collected data will serve as the basic input data for three-dimensional neutronic calculations. The specifications include the general description of the core, the main parameters of the fuel sub-assemblies, control rods and wrapper. The specific features of reflector and shielding fuel subassemblies are also given. The main material properties of uranium and plutonium dioxides and of non-fuel zone components (cladding and absorbing materials) were also specified. The main parameters of the steady-state reactor were identified.

The MTA EK contribution to the update of MOX catalogue included extensive review of new publications on the properties of fast reactor MOX fuel. The chapters “Thermal Expansion” and “Young Modulus” with the latest published results were produced by MTA EK experts.

## Remaining work

The project activities will be continued according to the original plans by 2017.

## Related publication

E. Temesvári: *ALLEGRO Core Specifications*, EK-FRL-2014-444-01/01, ESNII D6.1.1-2

### **III. HEALTH PHYSICS, SPACE DOSIMETRY**

# LINTEL SPACE DOSIMETRIC DETECTOR SYSTEM FOR PHANTOM MEASUREMENTS

A. Hirn, I. Apáthy, A. Csőke, S. Deme, J. Pálfalvi, T. Pázmándi, P. Szántó, B. Zábori

## Objective

The Centre for Energy Research, Hungarian Academy of Sciences (MTA EK) continues the activity of the KFKI Atomic Energy Research Institute in development of space dosimetry systems. The Pille system based on thermoluminescent dosimeters was dedicated for measurement of absorbed dose. The next step was the three-dimensional silicon detector telescope system TRITEL, capable of measuring the absorbed dose and the absorbed dose rate as well as the dose equivalent and dose equivalent rate in space. The objective of the development of linear telescope system LINTEL is the elaboration of a measurement system for estimating the effective dose to the astronauts due to heavy charged particles (LINTEL-P) and secondary neutrons (LINTEL-N) based on the technology (detectors and the corresponding signal and data processing units) used in TRITEL.

## Methods

Calculations were performed to determine the telescope geometry that can be used to determine the dose equivalent due to heavy charged particles for 5 critical organs (eye lens, testis, blood forming organs, central nervous system, gastro-enteric system) based on the depth distribution of dose and LET spectra in a human phantom. Given the geometry, the efficiencies of the detector pairs were also calculated for  $2\pi$  isotropic radiation.

The concept of a second detector head was elaborated for measurement of secondary neutrons provided that the signals coming from the detector head are processed by the same electronics as that by LINTEL-P, i.e. both detector heads share the very same signal processing unit.

Calculations for mass, data and power budgets were also performed.

## Results

The LINTEL-P detector head consists of three pairs of silicon detectors (telescopes). The detector thickness and the ratio of the detector diameter to the distance between the first two detectors are equivalent to the geometry of the TRITEL system to ensure compatibility of TRITEL and LINTEL measurements. The efficiencies of the second and the third detector pairs relative to the first one were found to be 0.17 and 0.37, respectively.

Due to the geometry of the system, the absorbers between the detectors shall have a significantly higher linear absorption coefficient than the tissue equivalent material of the phantom. As a consequence of this and also due to mechanical reasons, aluminium was found to be the proper material for the absorbent layers. Each of the 6 detectors in the LINTEL-P telescope serves both for spectrum measurement and for gating the spectra. Taking into account that only 3 analyzer channels are available in the electronic system, the function of the detectors in each detector pair is periodically interchanged with a period of 1 minute and the analyzers are used in time sharing mode. Using such a system, both the absorbed dose and the LET spectra can be measured at 6 different depths. From these spectra the dose equivalent can be calculated at different depths and hence the effective dose equivalent of ISS crew - members can be estimated.

The LINTEL-N detector head consists of two silicon detectors identical to the detectors in LINTEL-P and two  $^6\text{LiF}$  or  $^{10}\text{B}$  converter layers on two sides of the first silicon detector, which serves for measurement of neutrons thermalized in the phantom material. The second silicon detector - without converter layers - measures the primary charged particles and serves for compensation of these particles in the first detector. The difference in the integrated counts of LINTEL-N's neutron and charged particle detector and its compensation detector can be related to the fluence of neutrons below  $\sim 2$  MeV.

With minor modifications, the signal and data processing electronics of the TRITEL 3D silicon detector telescope is capable of processing the signals coming from both the LINTEL-P and LINTEL-N detector heads. Based on the first version of the technical specifications for a potential target experiment (the Matroshka-III anthropomorphic phantom experiment), the preliminary description of a feasible concept was provided [1].

## Remaining work

Providing a detailed design, manufacturing and testing of the system.

## Related publications

- [1] A. Hirn, I. Apáthy, A. Csőke, S. Deme, O. A. Ivanova, I. V. Nikolaev, J. Pálfalvi, T. Pázmándi, G. Shmatov, V. A. Shurshakov, P. Szántó, B. Zábori, *Preliminary description of the LINTEL system for phantom measurements*, Report, SVL-2014-121-01-01 (2014)



# DEVELOPING A NEW CONTAINMENT MODELLING CODE: HERMET2

*Attila Nagy*

## ***Objective***

In the last years different containment modelling programs were used at the Centre for Energy Research: CONTAIN code for the thermohydraulic phenomena and TIBSO for the activity transport within the containment. These codes are not integrated which makes it difficult to perform complex calculations. Our objective was to solve this problem by developing a new, integrated containment code which includes models from the fuel rod failure to the meteorological phenomena with the final goal to calculate the environmental consequences.

## ***Methods***

In our previous works [1] some physical models were developed; e.g. thermal hydraulic model for nodes, wall heat conduction model and reactor hall leakage model. These models are important parts of the new code but they must be integrated with the following ones:

- New fuel rod model based on the statistical and probability methods using available data from experiments and calculations
- Condensation model for wall films based on the Nusselt theory. This model is dealing with the presence of the non-condensable gases
- Wash-out model which calculates the sprinklers' wash out efficiency. This model takes into consideration the moving of the aerosol particles in the upper volume of the nodes
- Physical models of the valves and check valves
- Gas and hydrodynamics model for the junctions.

## ***Results***

For the above mentioned models the necessary literature has been collected and reviewed the diverse fields of physics such as thermo-dynamics, gas-dynamics, hydro-dynamics, cloud physics, etc.

The description of the models is given in [2] which contains a separate chapter dealing with computing aspects of the code as well.

The physical background of the new models is explained in [2], this document contains consideration about the working of the new models too. The inputs and outputs for the models are specified as well.

The comparison between junction transports calculated by the present code and CONTAIN code is still in progress.

In the application I wrote about the FLECS integration but there was no need for it. The FLECS is the programming language of the old simulator.

The SIMTONIA development is postponed. SIMTONIA is the framework of the new simulator which is under development in our institute.

## ***Remaining work***

Finish the CONTAIN comparison, start the SIMTONIA integration.

Implement the new models to the existing computer code.

## ***Related publications***

- [1] Attila Nagy: *Models and calculations about the accidental activity emission to the environment of the NPP Paks*, PhD thesis, 2014
- [2] Attila Nagy: *HERMET2 program plan ver 1.0* (in Hungarian), 2014

# MICROSCOPIC X-RAY FLUORESCENCE AND ELECTRON PROBE X-RAY MICROANALYSIS STUDY ON THE ND UPTAKE CAPABILITY OF ARGILLACEOUS ROCKS

*János Osán, Annamária Kéri, Margit Fábián, Felicián Gergely, Szabina Török*

## Objective

Argillaceous rocks are considered as suitable host rock formations for the deep geological disposal of high-level radioactive waste (HLW). The long-term safety of the HLW repository in a deep geological formation is influenced by the thermodynamic and geochemical parameters of the host rock formation. Therefore, the determination and quantification of geochemical and physical processes that influence the mobility of the radionuclides in the deep geoenvironment imposed by the host rock is indispensable. In the present study, the interaction between the host rock surrounding the planned HLW repository and Nd(III) ion representing trivalent transuranium elements from the HLW was studied. Core samples were taken and prepared from Boda Claystone Formation (BCF), which is the most suitable geological formation for the planned HLW repository in Hungary. Due to the high heterogeneity of argillaceous rocks on the microscale, microscopic techniques with sufficient sensitivity were necessary to examine the radionuclide uptake processes without the necessity of the application of radioactive substances. Therefore, synchrotron radiation based microscopic X-ray fluorescence (SR micro-XRF) and electron probe microanalysis (EPMA) measurements were carried out on the treated samples. The two microanalytical methods delivered supplementary information about the elemental distribution of the samples. Major elements with low atomic numbers representing the mineral phases of the host rock could be determined using EPMA, while neodymium present at trace level could be detected by micro-XRF. Multivariate methods were found to be efficient tools for extracting information from the elemental distribution maps. Positive matrix factorization (PMF) and cluster analysis (CA) were applied on these large data sets to gain information about the neodymium uptake capacity of the mineral phases. The outcome of the multivariate methods was compared with microscopic X-ray diffraction (micro-XRD) results.

## Methods

Thin sections were prepared from representative core samples selected from two areas of BCF, i.e. West-Mecsek Anticline Block (Sample D-11) and Gorica Block (Sample Ib-4). The thin sections were subjected to 72 hour uptake experiments with Nd(III) ion added using 0.1 M NaCl solution as background electrolyte.

A JEOL JSM05600LV scanning electron microscope (SEM) equipped with an Oxford Si(Li) energy dispersive detector with atmospheric thin window was employed for the EPMA measurements. Elemental maps with a resolution of  $4.5 \times 4.8 \mu\text{m}^2$  were recorded at a 25 kV accelerating voltage and a 1 nA beam current. In order to decrease sample damage due to the electron beam, the area was scanned ten times with a 150 ms dwell time at each position. The concentrations of major elements were determined for each pixel of the elemental maps using an irregular iterative method based on Monte Carlo simulations for electrons.

The micro-XRF/XRD experiments were performed at the FLUO beamline of ANKA applying monochromatic excitation at a primary beam energy of 7.0 keV ( $\Delta E/E = 10^{-2}$ ). The beam was focused to a spot size of  $3 \times 5 \mu\text{m}^2$  using a Fresnel zone plate. Elemental maps were recorded for the adsorbed element (Nd) as well as for the major and minor elements of the rock measurable by XRF (e.g. K, Ca, Fe, Rb, Sr), using a  $5 \mu\text{m}$  step size and 4–10 s counting time per pixel. The elemental concentrations were calculated using the fundamental parameter method, taking into account the thickness of the sample ( $50 \mu\text{m}$ ) and the average density of the rock ( $2.7 \text{ g/cm}^3$ ). Several micro-XRD images were collected by a 130 mm diameter CCD detector from selected positions of interest.

The interleaving of micro-XRF and EPMA data sets was prepared for further evaluation based on the potassium and calcium elemental maps recorded using both methods. Factor analysis (FA), positive matrix factorization (PMF) and cluster analysis (CA) were applied for evaluation of the combined data set.

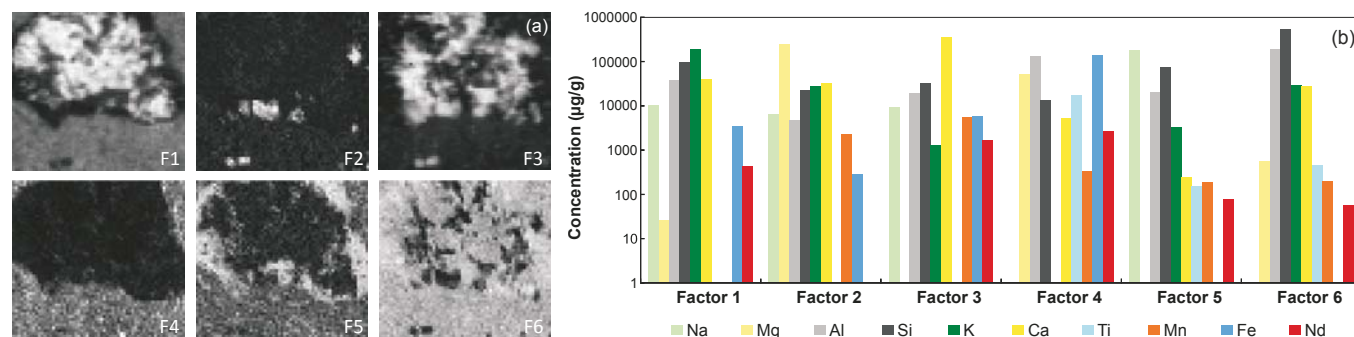
## Results

Multivariate methods applied on interleaved micro-XRF and EPMA elemental maps contained sufficient information to entirely identify the main mineral phases responsible for the uptake of Nd(III). The ion binding capability of the different mineral phases could be estimated by performing PMF on the interleaved data set. The Nd uptake capability of the clayey matrix (Fig. 1) could be evaluated as  $1200 \mu\text{g/g}$ . Almost the same amount of Nd ( $1100 \mu\text{g/g}$ ) was bound to a calcium rich mineral phase representing calcite while the ion uptake capability of dolomite was significantly lower (Fig. 1). It should be highlighted that the ion uptake capability of dolomite containing calcium and magnesium could be distinguished from the very diverse characteristics of calcite only by the interleaving of micro-XRF and EPMA data sets. For both mineral phases non-negligible, as different amount of manganese was bound corresponding to the two-phase manganese-carbonate.

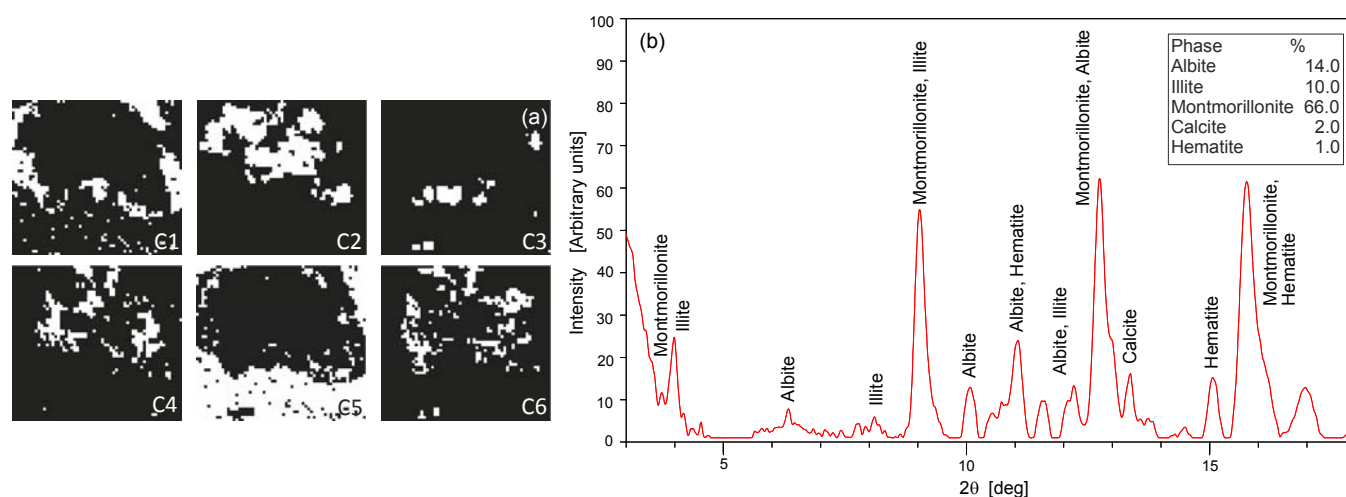
Cluster analysis was carried out also on the interleaved micro-XRF and EPMA data set taking into account only those elements which were dominant in the factors obtained as the result of PMF. The mineral phases and mineral aggregation could be identified and their ion binding capability could be estimated as the result of CA. There were two separable clusters which appeared on the edge of the calcites and/or aluminosilicates which had the highest neodymium binding capability with an average neodymium content of  $1460 \mu\text{g/g}$  and  $1140 \mu\text{g/g}$  (Fig. 2a). It seems to be in contradiction with the PMF results. This was because neighbouring pixels at the border could also contain non-negligible amount of calcite. CA classified

them into a separate cluster while PMF takes into account their higher deviation and classifies them to the factor representing the clayey matrix or the calcite. As a fact, the amount of neodymium bound to the clayey matrix was found to be lower.

Inspecting positions representative for the clayey matrix by micro-XRD, Nd content was in a good correlation with the clay mineral (illite and montmorillonite) content indicating the importance of these minerals in the Nd uptake of the rock (Fig. 2b). At the positions of high Nd content in the fracture infilling region of the scanned sample area, calcite was found in high concentration while dolomite was not detected, in accordance with the PMF and CA results.



**Figure 1:** Factor contribution maps (a) and profiles expressed as elemental concentrations (b) for selected area of a D-11 sample treated with Nd(III) (c). The results were obtained performing PMF on the interleaved data set of EPMA and micro-XRF data set.



**Figure 2:** (a) Cluster maps for the same selected area as shown in Fig. 1, obtained using CA on the interleaved data set of EPMA and micro-XRF, (b) 1D micro-XRD pattern for a position of high Nd content in the clayey matrix

## Remaining work

Comparison of macroscopic and microscopic studies of the uptake representative ions by BCF, with verification of the uptake mechanism applying X-ray absorption spectrometry techniques.

## Acknowledgement

The research leading to these results has received funding from the Swiss-Hungarian Cooperation Programme through Project n° SH/7/2/11. We acknowledge the Synchrotron Light Source ANKA for provision of instruments at their beamlines and we would like to thank Rolf Simon for his great help. The courtesy of the Public Limited Company for Radioactive Waste Management (PURAM, Hungary) for providing the samples for analysis is also appreciated.

## Related publications

- [1] A. Kéri, J. Osán, M. Fábián, R. Dähn, S. Török; *Microscopic X-ray fluorescence and electron probe X-ray microanalysis study on the Nd uptake capability of argillaceous rocks*, X-ray Spectrometry, submitted
- [2] J. Osán, A. Kéri, D. Breitner, M. Fábián, R. Dähn, R. Simon, S. Török; *Microscale analysis of metal uptake by argillaceous rocks using positive matrix factorization of microscopic X-ray fluorescence elemental maps*, Spectrochimica Acta Part B, 2014, vol. 91, pp. 12-23
- [3] D. Breitner, J. Osán, M. Fábián, P. Zagyvai, C. Szabó, R. Dähn, M. Marques, I. Sajó, Z. Máthé, S. Török; *Effect of mineralogical characteristics on the U(VI) uptake of Boda Claystone Formation as the candidate host rock of high activity and long lived nuclear waste repository in Hungary*, Environmental Earth Sciences, 2015, vol. 73, pp. 209-219

# ASSESSMENT OF RADIATION SITUATION AND DEVELOPMENT OF LONG-TERM MEASURES BASED ON METEOROLOGICAL DATA AND MEASUREMENT INFORMATION OF OSJER

## PART I.

*Lilla Hoffmann, Emese Homolya, Tamás Pázmándi, Péter Szántó,  
Márton Zagyvai, Péter Zagyvai*

### **Objective**

The aim of the project was to develop a strategy for the evaluation of the radiation situation and the long-term protective measures in the late phase of an emergency, to determine the environmental generic intervention levels and to review the available measurement data in the present operative systems. We investigated the available measurement capacity in case of an emergency situation.

### **Development proposals**

For the construction of a calculation method, the determination of the operational intervention levels (OILs) for the Hungarian relations is necessary. Radiological measuring capacity of Hungarian organizations were summarized, measuring capacity of the individual systems in normal operational and emergency situations were evaluated.

Suggestions for further development were summarized. In order to reveal calculation methods for the OILs defined in the new IAEA publications, consultations with the Incident and Emergency Centre of IAEA were suggested. Measurement data should be collected in one standard database. To optimize data collection, measuring methods should be standardized and the data format and sending frequency should be determined. Usage of the IRIX format is suggested. Taking emission and meteorological data into account is also recommended. For the fast radiological survey of the area surrounding the emission source, additional valuable data can be obtained by the use of installed measuring instruments on drones.

### **Remaining work**

In the further work the construction of a software that is capable of the visualization of measured data on maps and makes suggestions for the introduction of protective measures based on the environmental intervention level is planned.

### **Related publication**

L. Hoffmann, E. Homolya, T. Pázmándi, P. Szántó, M. Zagyvai, P. Zagyvai: *Assessment of radiation situation and development of long-term measures based on meteorological data and measurement information of OSJER*, report, EK-SVL-2014-262-01-01-01 (2014)

# ACCEPTANCE CRITERIA FOR SAFETY ANALYSES: APPLICATION OF ATMOSPHERIC RELEASE CRITERIA

## -PART 1

*Emese Homolya, Péter Szántó, Tamás Pázmándi*

### **Objective**

In order to eliminate uncertainties from the modeling of environmental transport, it has been stated in the latest years that emission criteria should be used for the limitation of environmental effects in the area of nuclear facilities. For this aim, introduction of the criteria should be investigated, methods suitable for the determination of criteria for nuclear facilities should be analyzed for design basis incidents and beyond design basis incidents, and conditions for the application in practice should be stated. This work was prepared in the frame of the OAH-ABA-61/13-M contract on release criteria applied in safety analyses.

### **Methods**

In the first year of the four-year-long project four tasks were accomplished. The Hungarian regulations on deterministic safety assessments related to airborne radioactive releases were summarized. The European Utility Requirements (EUR) document published by European nuclear power plant operators and reports published by the International Atomic Energy Agency (IAEA) and the United States Nuclear Regulatory Commission (US NRC) on acceptance criteria for airborne radioactive releases were overviewed. The basis of a method in agreement with the Hungarian legal environment and international recommendations was established. Calculations and sensitivity assessments were performed in order to determine which parameters play more and which are less important parts in the results.

During the work, criteria for both design basis and beyond design basis incidents were considered. Criteria for the public population were analyzed, but the regulations for on-site dose burden were not assessed. However, the methods described in the report can be applied for on-site conditions with only minor modifications.

The results of elaboration of regulations for deterministic assessments performed simultaneously were also considered.

### **Results**

For the investigation on atmospheric emission criteria we made a review of the national regulation environment and practice carried out in the latest years as a first step. We summarized the relevant parts of the Nuclear Act CXVI of 1996, the EüM Decree No. 16/2000, the Nuclear Safety Regulation and the Final Safety Analysis Report of Paks Nuclear Power Plant. We concluded that on the one hand, neither the requirements are obvious, nor clear guidance for the application exists in practice. On the other hand, the Hungarian practice can be stated to be more or less standard, that is to be put down to the fact that analyses have been made by the same group for decades, using the same tools. However, some deviations do exist.

The EUR requirements, documents of US NRC, publications of the International Atomic Energy Agency and the EU BSS have been reviewed. According to the information available, there is no standard routine for emission criteria used in safety analyses in the neighbouring countries. Applied systems in the individual countries have been worked out based upon international recommendations; they harmonize with the recommendations, however, considerable deviations exist.

Based on the Hungarian and international practice and protocols, it can be stated that a standard routine for atmospheric release criteria applicable for safety analyses does not exist. We made an investigation on the factors that may considerably affect the values of parameters used in dose calculations. Emission height, precipitation, wind speed, Pasquill category, building dimensions, integrating time and dose conversion factors have been examined.

### **Remaining work**

In the next year of the project, in agreement with the four years plan, the site parameters of Hungarian nuclear facilities, which play important role in determining the release criteria, have to be defined. Later the details of the method suggested in the report will be elaborated and the values of the coefficients will be calculated. In this task the following points shall be considered: results shall be in agreement with the international recommendations and the current assessment results, and methods shall be applicable in the long term without frequent modifications. The final goal of the project is to create a draft version of guidelines on application of the release limits.

### **Related publications**

- [1] E. Homolya, T. Pázmándi, P. Szántó: *Acceptance criteria of safety analyses: application of atmospheric emission criteria – Part 1*, Version 1, Report, EK-SVL-2013-284-01-01-00 (2014)
- [2] E. Homolya, T. Pázmándi, P. Szántó: *Acceptance criteria of safety analyses: application of atmospheric emission criteria – Part 1*, Version 2, Report, EK-SVL-2013-284-01-01-00 (2014)

# REM-RED STRATOSPHERIC SOUNDING ROCKET EXPERIMENT TO MEASURE THE COSMIC RADIATION WITH GM-COUNTERS

*Balázs Zábori, Attila Hirn, Tamás Pázmándi, István Apáthy, András Gerecs*

## Objective

The REM-RED experiment is designed to perform measurements with active radiation instruments (GM-counters) in order to quantify the cosmic radiation field from the Earth's surface up to the maximum altitude of the REXUS rocket (80-100 km).

## Methods

Based on the earlier experiences on the Hungarian BEXUS missions and that of the Hungarian space researchers, the development of a highly reliable cosmic radiation measuring platform for sounding rockets got underway.

There are several ways to measure the cosmic radiation; however, it is not easy to apply them to a sounding rocket meeting the high level of environmental requirements. The easiest way is to use GM-counters to quantify the radiation level. The main design goals are as follows: high radiation sensitivity, direction sensitivity, high reliability, safety and the possible future use. The high radiation sensitivity will be achieved using higher sensitive volume and increasing the number of GM-counters included in the experiment. 4 ZP1210 type tubes will be used for the measurements. 2 ZP1200 type tubes with significantly lower sensitivity will be included for testing purposes. These GM tubes, however, can play significant role in future rocket missions where the mass and the volume are critical and limited.

The REXUS/BEXUS programme is realised under a bilateral Agency Agreement between the German Aerospace Center (DLR) and the Swedish National Space Board (SNSB). The Swedish share of the payload has been made available to students from other European countries through a collaboration with ESA (European Space Agency). EuroLaunch, a cooperation between the Esrange Space Center of the Swedish Space Corporation (SSC) and the Mobile Rocket Base (MORABA) of DLR, is responsible for the campaign management and operations of the launch vehicles.

## Results

In year 2014 the REM-RED experiment design work passed the following reviews that were absolutely necessary in order to get a "Go ahead" for the REXUS-17 rocket flight in spring 2015, namely the Preliminary Design Review, the Critical Design Review, the Experiment Acceptance Review and the Final Experiment Integration Review.

The experiment's mechanical design has been completed in agreement with the REXUS rocket mechanical interface and requirements, based on several mechanical/thermal simulation results. The final mechanical structure was built (Fig. 1). The qualification model of the electronics system has been built and tested in all details. The flight model electronics system was included into the final mechanics. The REM-RED Electrical Ground Support System (EGSE) has been designed and built to permit simulation of the flight sequence of the REXUS rocket. A detailed experiment acceptance level test campaign was defined and carried out in order to verify the mission requirements. No major failures or critical points were identified; the experiment passed all acceptance test levels

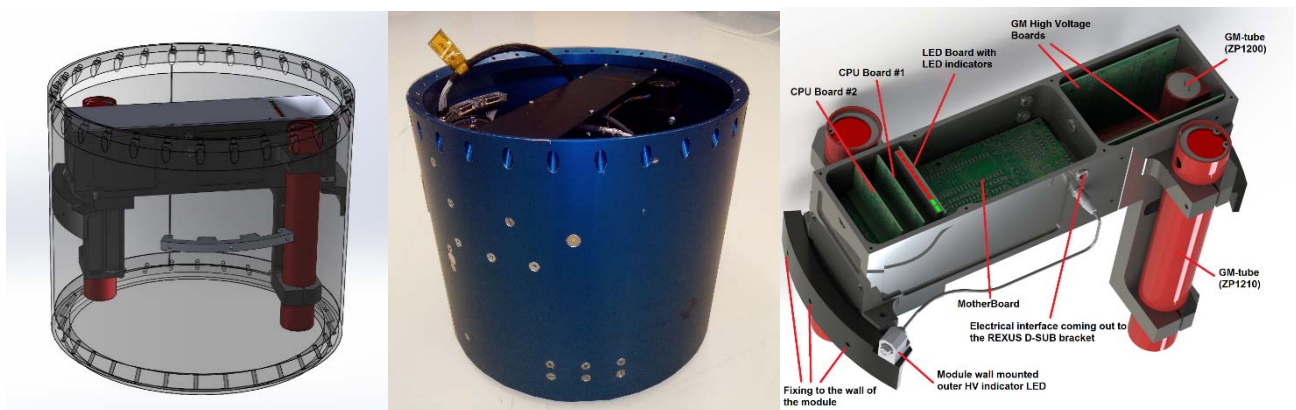


Figure 1: The REM-RED experiment in the REXUS rocket module

## Remaining work

At the beginning of 2015 the final Bench Test of the REXUS 17 rocket will take place. After this test the experiment will be shipped to the Esrange Space Center (Kiruna, Sweden) for the Launch Campaign. The expected date for the Launch Campaign is between from the 8<sup>th</sup> and the 21<sup>st</sup> of March 2015. The final results should be presented at the usual ESA balloon and rocket symposium (PAC Symposium) during the summer of 2015.

## Related publication

B. Zábori: REXUS REM-RED Student Experiment Documentation, RX17\_REMRED\_SEDv4-0\_31Oct14 (2014)



# DEVELOPMENT OF THE TRITEL SATELLITE VERSION SILICON DETECTOR TELESCOPE FOR THE ESEO MISSION

*Balázs Zábori, Attila Hirn, Tamás Pázmándi, István Apáthy, András Gerecs*

## Objective

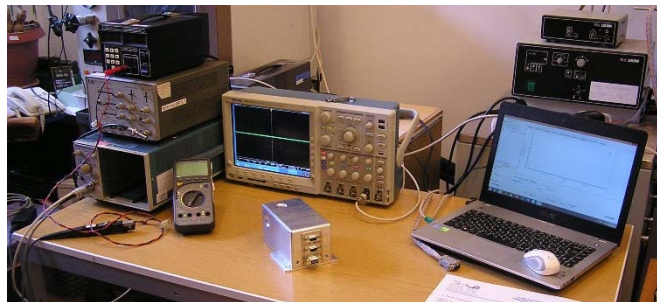
The mission objectives of the ESEO (European Student Earth Orbiter) project are given in the statement of work document of the ESEO program. It is clearly stated in the documentation that one of the ESEO mission objectives is to measure the ionizing radiation environment in orbit. The ESEO-TRITEL student team is responsible for the design and the building of an instrument for cosmic radiation experiments. The experiment will focus on the cosmic radiation in the near-Earth region, especially in the South Atlantic Anomaly and in the Polar regions, on the variations in space weather and the effects of solar activity on the Earth's magnetic field.

## Methods

The principle of TRITEL is the radiation quality assessment based on deposited energy (linear energy transfer) spectra measurements. The instrument is a three-dimensional silicon detector telescope comprising six identical fully depleted passivated implanted planar silicon detectors and designed to measure the energy deposit of charged particles. In each telescope axis, the first detector (closer to the outer box) is the measuring detector and the second one is the gating detector; the three axes are mutually orthogonal to each other. In the frame of the work a specific, satellite version of the TRITEL silicon detector telescope has to be designed and built based on ESEO and ESA (European Space Agency) general satellite mission requirements. The ESEO satellite will be injected to 520 km polar orbit, which makes it possible to study the radiation environment around the poles of the Earth as well. The planned mission time is six month; which can be extended with two more years.

## Results

In year 2014 the ESEO-TRITEL payload design work passed the following reviews that were absolutely necessary in order to get a "Go ahead" for the ESEO satellite mission in spring 2016, namely the Preliminary Design Review and the first part of the Critical Design Review. The experiment mechanical design has been completed in agreement with the ESEO satellite mechanical interface and requirements, based on several mechanical/thermal simulation results. The prototype of the mechanical assembly has been manufactured. A detailed Verification and Test Plan has been provided together with several Test Procedures and accepted by the coordinators of the ESEO satellite mission (ALMA Space and ESA). The electrical design of the original TRITEL instrument was totally reviewed and some modifications were applied to fulfil the ESEO electrical and interface requirements. New power supply board was designed and approved by the ESA experts based on the high level of ESA requirements (Fig. 1). [1-5]



*Figure 1: The first qualification tests with the ESEO-TRITEL payload*

## Remaining work

The work continues with closing the Critical Design Review. After the successful approval of all deliverables the Engineering Qualification model will be built and tested for qualification level in order to ship it to the ALMA Space at the end of April 2015. The Flight Model will be provided and tested for acceptance test level until the end of September 2015. At the end of 2015 a detailed operation plan has to be defined for the ESEO-TRITEL payload.

## Related publications

- [1] B. Zábori: *ESEO-TRITEL Design Definition File*, AS-12\_0005-TRITEL-DDF-01\_v2.1 (2014)
- [2] B. Zábori: *ESEO-TRITEL Experiment Interface*, AS-12\_0005-TRITEL-EIDB-01\_v2.2 (2014)
- [3] B. Zábori: *ESEO-TRITEL Test Plan*, AS-12\_0005-TRITEL-TP-01\_v2.5 (2014)
- [4] B. Zábori and ESEO-TRITEL Team: *Qualification ESEO-TRITEL input power test procedure*, MTA EK-SVL-2014-352-01-05A-07 (2014)
- [5] B. Zábori and ESEO-TRITEL Team: *ESEO-TRITEL mechanical simulation results*, MTA EK-SVL-2014-352-03-01-02 (2014)



# THREE DIMENSIONAL DOSE MAPPING INSIDE THE ISS

*Andrea Strádi, József K. Pálfalvi, Julianna Szabó*

## Objective

The new DOSIS-3D experiment in the frame of an European Space Agency programme lead by the German Aerospace Center (DLR) with the participation of nine countries started in 2012. The aim of the project was to create a three dimensional dose distribution data base for the European Columbus Laboratory of the International Space Station (ISS).

## Methods

Thermoluminescent detectors (TLD) and solid state nuclear track detectors (SSNTD) were applied by the MTA EK Space Dosimetry Group to investigate the dose contribution of the low ( $< 10 \text{ keV}/\mu\text{m}$ ) and high ( $> 10 \text{ keV}/\mu\text{m}$ ) Linear Energy Transfer (LET) cosmic radiation. The plastic detector boxes consisted of two SSNTDs and six TLDs (half of them was made of  $^6\text{Li}$  enriched MTS-6 material, the other half was  $^7\text{Li}$  enriched MTS-7). In each phase there were thirteen boxes in eleven fixed locations (ten single boxes and a set of three boxes, arranged in the three directions of space) inside the module (see Fig. 1). This report contains the evaluated data of the TLDs from the fifth phase.

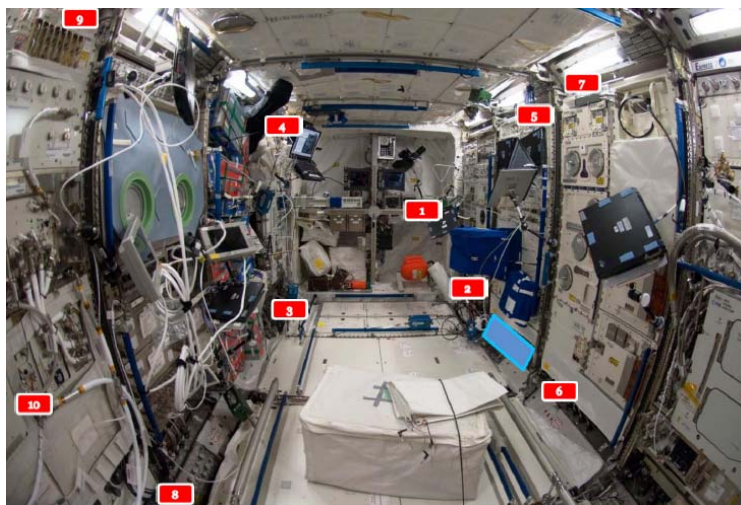


Figure 1: Interior of the Columbus module on the ISS. The single locations are numbered from 1 to 10, the three directional set is marked with a blue rectangle.

## Results

The detectors of the fifth phase of DOSIS-3D were exposed during the period between March 25 – September 11, 2014. Results obtained by the different participants with the two types of TLDs in the eleven locations are shown in Fig. 2.

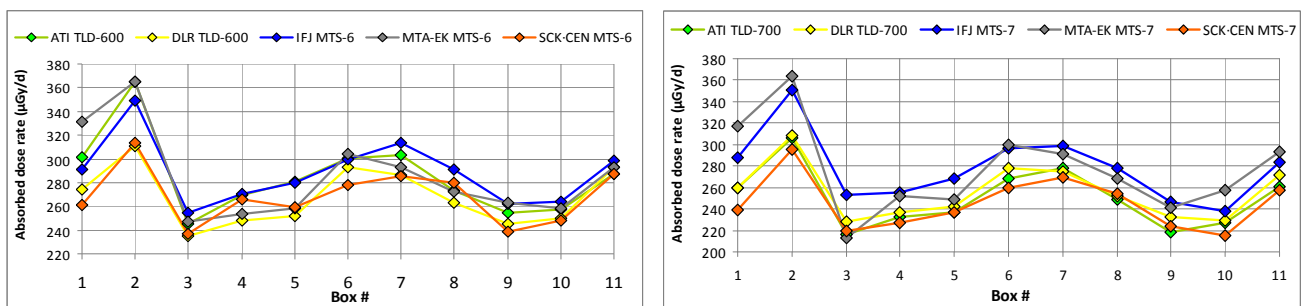


Figure 2: Absorbed dose rates in  $\mu\text{Gy}/\text{day}$  of the low LET part ( $< 10 \text{ keV}/\mu\text{m}$ ) of cosmic radiation in the different boxes during DOSIS-3D/5 phase. Left: MTS-6 type TLDs. Right: MTS-7 type TLDs.

All participants measured the same characteristic of dose distribution, which depends not only on the local thickness of the shielding material but also on the orientation of the module due to the west-to-east anisotropy of the protons trapped by the Earth's geomagnetic field. The latter effect was well demonstrated by comparing the dose rates in locations 2 and 3. The mean standard deviation over the 11 averaged data of the participants was 5.5%, which reflects a good agreement, although the detector materials and evaluation methods were different. The doses measured with detectors enriched in  $^6\text{Li}$  were always higher, proving the presence of low energy, secondary neutrons generated by high energy galactic cosmic rays.

## Remaining work

The evaluation of the SSNTDs is still in progress and planned to be completed in early 2015.

# COSMIC RAY STUDIES ON THE BION-M1 SATELLITE

József K. Pálfalvi, Andrea Strádi, Julianna Szabó

## Objective

In the frame of a scientific co-operation between the Russian Institute for Biomedical Problems (IBMP) and MTA EK in 2013 several cosmic ray detectors were exposed, in the one-month Bion-M1 satellite program, to study the radiation field inside and outside of the descent module during the flight. The aim of the numerous physical and biological experiments on the satellite was to support the preparation for manned interplanetary missions in the near future. The spacecraft was launched from Baikonur, Kazakhstan on the 19<sup>th</sup> April, orbiting the Earth at 575 km altitude, with an inclination of 64.9° for 30 days.

## Methods

The MTA EK detector packages included thermoluminescent (TLD) and solid state nuclear track detectors (SSNTDs). By these combined detector stacks the low and high linear energy transfer (LET) components could be determined separately. TLDs are sensitive in the low LET range, under  $10 \text{ keV } \mu\text{m}^{-1}$ , whereas SSNTDs measure the different high LET components (protons and energetic charged particles) of the galactic cosmic ray and the secondary fragments generated by these particles while passing through the surrounding material of the spacecraft, integrated over the whole flight, from 10 up to  $1000 \text{ keV } \mu\text{m}^{-1}$ . There were detector packages inside the module, positioned vertically and horizontally in the storing boxes made of aluminum. Three of these boxes were placed next to the corners of the internal platform and one in the middle (box No. 2), surrounded by payloads. Outside the satellite two of the open-to-space external holders were occupied by aluminum boxes with passive detector packages parallel to the surface of the module. In 2014 all obtained results were evaluated and compared to those ones measured inside the International Space Station (ISS, altitude ~400 km, inclination 62°) nearly in the same calendar interval, and outside the satellites of the previous Foton-M2 and -M3 missions.

## Results

Both of the dose rates measured by TLDs ( $\text{LET} < 10 \text{ keV } \mu\text{m}^{-1}$ ) and SSNTDs ( $\text{LET} > 10 \text{ keV } \mu\text{m}^{-1}$ ) showed strong location dependence, due to the different shading conditions. The lowest absorbed dose rates were obtained in the most shaded location inside the capsule (2h and 2v in Fig. 1.). The highest doses were detected by TLDs, in the external containers (e1 and e2 in Fig. 1., left), since TLDs have greater sensitivity to the low-energy particles, being present in large quantities in the free space, but rapidly absorbed by the structural materials of the module.

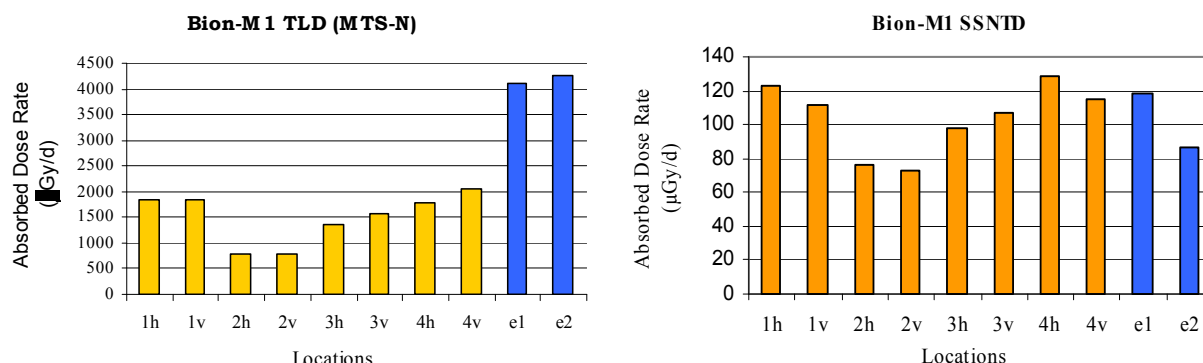


Fig. 1. Left: Absorbed dose rates measured by TLDs inside (with yellow) and outside (with blue) of the module in different locations. Right: Dose rates measured by SSNTDs inside (with yellow) and outside (with blue) of the module in different locations.

The measurements by SSNTDs revealed that the doses from high LET components inside and outside the satellite were in the same range (see Fig. 1., right), but the average particle fluxes were higher outside the satellite, as expected. During nearly the same period there were two consecutive dosimetry projects with the participation of MTA EK on board the ISS, under the name of TRITEL-SURE (October 2012 – May 2013) and Dosis 3D/3 (March – September 2013). The doses measured inside the Bion-M1 satellite were more than twice as high as on the ISS, mostly due to the biosatellite's higher altitude. Similarly, most of the dose values were higher in comparison with the measurements taken on the outer surface of the Foton-M2 in 2005 (255 km x 304 km orbit) and Foton-M3 in 2007 (258 km x 280 km orbit), due to the altitude differences [1].

## Remaining work

In 2015 the results will be published in the conference proceedings of the XV. Conference on Space Biology and Aerospace Medicine based on the presented material.

## Related publication

A. Strádi, J. K. Pálfalvi - MTA EK: Biosatellite Experiments (in Hungarian), Műszaki Szemle - Technika 2014/10, 34-36, HU-ISSN 0040-1110

# MEASUREMENTS ON BOARD THE INTERNATIONAL SPACE STATION WITH THE TRITEL 3D TELESCOPE

*Attila Hirn, István Apáthy, Antal Csőke, Sándor Deme, József K. Pálfalvi, Tamás Pázmándi, Péter Szántó, Balázs Zábori*

## Objective

In 2014 the main objective of the project was to provide a comprehensive analysis of measurement data obtained on board the European Columbus and the Russian Zvezda module of the International Space Station (ISS) by the three-dimensional silicon detector telescope system TRITEL, developed at MTA EK in cooperation with BL-Electronics Ltd. The TRITEL instrument is capable of measuring not only the absorbed dose in the cosmic radiation field, but also the linear energy transfer (LET) spectrum of the charged particles and their average quality factor in three mutually orthogonal directions in order to give an estimation of the equivalent dose, too. Another important task was to conduct troubleshooting tests on the TRITEL Interface Unit (IU) retrieved from the Russian Segment of the ISS as well as to repair and test the unit for further use on board the space station.

## Methods

After data evaluation, TRITEL results obtained were compared with results from other detector systems on board the ISS. Data gained from ground calibration measurements at high energy particle accelerators were also compared. Correlation analyses of measurement data with orbital parameters and solar activity were performed as well.

Tests were run on different IU memory units (the boot flash, the NOR flash, the SDRAM, and the CF memory card unit). Data content of the memory units was checked and compared with the back-up files created before delivery to the ISS.

## Results

A deviation in the shape of the measured energy deposition spectra was identified compared to measurements with other detector systems on board the ISS. Calculations and tests were performed to figure out what the reasons might be. Unfortunately the behaviour, at the moment, is still not completely understood. Comparison of calibration data with other dosimeter telescope systems is on-going. No indications of solar events (like Coronal Mass Ejections) were identified in the TRITEL measurement data. The altitude of the ISS changed within 10% and the daily mean altitude was practically constant (410 km; change was less than 1%) during the mission. No correlation was found between the altitude of the ISS and either the trapped or the not trapped component of the cosmic radiation. Significant effects on the measured count rates as well as on the 90-minute SAA spectra could be observed due to the difference in the shielding configuration as the International Space Station enters the SAA either on the ascending or the descending part of its orbit.

Origin of the problem with the Russian TRITEL IU could not be determined. No hardware deficiencies or hard errors in the memory units were found. It was proven that the 2<sup>nd</sup> partition on the CF Memory Card was affected; the errors could be repaired with running a file system consistency check. The SDRAM might also have been affected; a possible soft error in the SDRAM might have corrupted the content on the 2<sup>nd</sup> partition on the CF Memory Card. Nevertheless, this assumption cannot be studied posteriorly. The internal controller of the CF Memory Card might also have been affected that might have corrupted the content on the 2<sup>nd</sup> partition on the CF Memory Card. The probability that any other units caused the problem is very low [1]. The reliability of the Interface Unit has been increased by changing the CF memory card with an industrial CF card dedicated for critical program storage with much more effective error correction. The file check performed during the boot process was set to "forced yes to all" in order to prevent the system waiting for user interaction. The tests necessary before delivery have been performed [2-3].

## Remaining work

The maintenance of the TRITEL system on board the Russian segment of the ISS, as well as the analysis of measurement data coming from the space station will continue in the coming years.

## Acknowledgements

The TRITEL-SURE experiment was co-funded by the EC project SURE, contract number RITA-CT-2006-026069 and by the Government of Hungary through ESA Contracts 98057 and 4000108072/13/NL/KML under the PECS (Plan for European Cooperating States). TRITEL-RS is operated on board the Russian Segment in frame of the Matroshka-R space experiment in cooperation with the State Scientific Center, Institute for Biomedical Problems, Russian Academy of Sciences, Moscow and it was funded by the National Development Agency (contract number URKUT\_10-1-2011-0036). The authors wish to acknowledge the precious help provided by the colleagues at IBMP and RSC Energia.

## Related publications

- [1] A. Hirn, I. Apáthy, P. Szegedi: *TRITEL-RS Interface Unit FM Failure Analysis*, report, EK-SVL-2014-405-05-01-00 (2014)
- [2] A. Hirn: *TRITEL-RS Interface Unit FM Software Functional Test Procedure*, report, EK-SVL-2014-405-05-02-00 (2014)
- [3] A. Hirn: *TRITEL-RS Interface Unit FM 2 Acceptance Test – Protocol #2*, report, EK-SVL-2014-405-05-03-00 (2014)

# DUST AND PLASMA MEASUREMENTS ON COMET 67P/C-G

*István Apáthy, Attila Hirn, Attila Péter, Balázs Zábori*

## Objective

European Space Agency's space probe *Rosetta* is the first spacecraft ever designed to orbit and land on the nucleus of a comet. The objective of the mission is to study the origin of comets and the relationship between cometary and interstellar material and its implications with regard to the origin of the Solar System.

## Methods

The *Rosetta* mission was launched in 2004 for studying the comet 67P/Churyumov-Gerasimenko (67P/C-G) in-situ for at least one year, from the onset of activity beyond 3 AU to perihelion. The spacecraft carried a lander called *Philae*, a small, compact laboratory to be released onto the icy surface of 67P/C-G. MTA EK is participating in two of the nine scientific experiments aboard the Lander. The first one, *DIM* (Dust Impact Monitor) is a part of the small instrument package *SESAME* (Surface Electrical, Seismic and Acoustic Monitoring Experiments) for determining the mechanical and electrical properties of the comet's surface; the second one, *SPM* (Simple Plasma Monitor) is a part of another small instrument package known as *ROMAP* (Rosetta Lander Magnetometer and Plasma Monitor) which complements the plasma packages on board the *Rosetta Orbiter*. The *DIM* acoustic dust detector will investigate the material that impacts and falls on the nucleus of the comet; the *SPM* sensor is capable of measuring the major solar wind parameters as a function of the distance from the Sun.

The piezoelectric sensors of *DIM*, located outside the *Lander*, with active surfaces looking into three orthogonal directions, were designed to detect the impacts of particles having energies in the range of  $10^{-11}$  J ...  $10^{-7}$  J. The sensor's electric output signals of broad dynamic range are amplified by wide-band logarithmic amplifiers. The characteristics of the impact signals (peak amplitudes, half-contact time, average) are measured by an appropriate electronic circuit, connected to the common Data Processing Unit (DPU) of *SESAME* by a digital bus-system.

The *SPM* sensor is a type of electrostatic, hemispherical analyser having 2 ion channels and 1 electron channel. It contains a Faraday cap as well. The energy range of the instrument is 0-12.6 keV for ions with a resolution of 3%, and 0-4.5 keV for electrons with a resolution of 10%; the field of view of the sensor is  $140^\circ \times 150^\circ$  for ions and  $8^\circ \times 15^\circ$  for electrons. The sensors of *ROMAP* are mounted on the end of a short boom and are coupled to a small DPU to store data and control the power consumption in modes with reduced data rates.

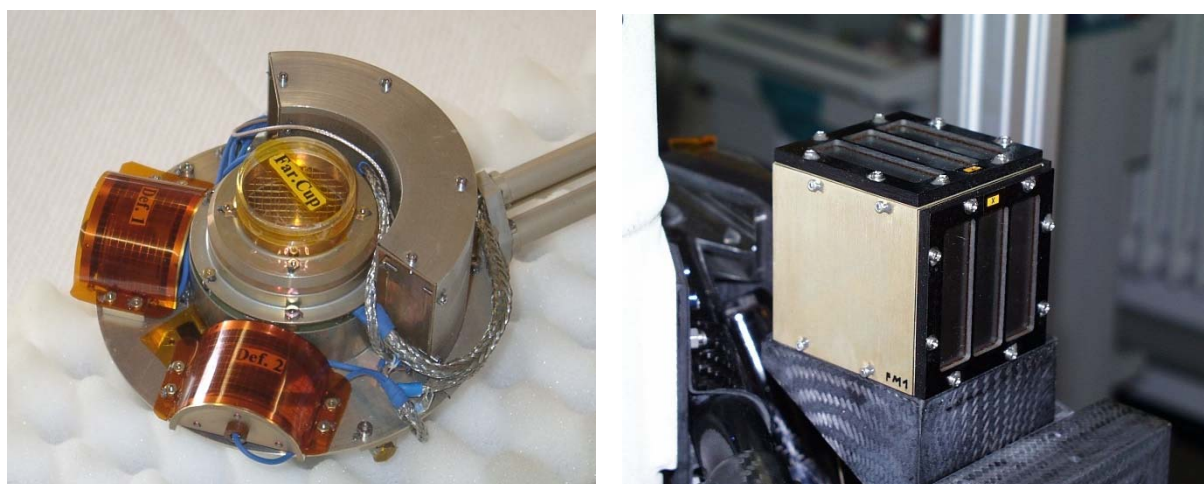


Figure 1: Detectors of the SPM on the end of the ROMAP boom and the DIM sensor on the balcony of the Lander

## Results

In June 2011 the *Rosetta* spacecraft was switched off for a longer period in the Deep-Space Hibernation (DSH) phase of its orbit. Its switch-on was performed in January 2014 while the commissioning and first check-out of the *Lander* instruments after hibernation were conducted in May 2014. *Rosetta* reached its target 67P/C-G on the 6<sup>th</sup> of August; landing of *Philae* took place on the 12<sup>th</sup> of November 2014.

MTA EK experts were continuously taking part in data archiving and planning the operation during descent and the first scientific measurements as well as in the landing site selection process. All operations on the flying *Lander* were first tested on the identical Ground Reference Model (GRM) at the German Aerospace Center (DLR) in Cologne, Germany. Keeping in operation of the GRMs of both the *SESAME* and the *ROMAP* instrument packages continued.

In April 2014 the Post-Hibernation Commissioning (PHC) of the *Lander* was conducted. The evaluation of the data achieved during the commissioning proved the proper operation of the instruments in *SESAME* including *DIM*. Temperature dependence tests and an interference test during APXS operation were also performed. The *DIM* instrument detected no interference. The *ROMAP* switch-on test, the Extended Abbreviated Function Test and the *ROMAP* SPM High Voltage tests proved the proper operation of *ROMAP* including *SPM*. *ROMAP* was used as an indicator during the APXS Deployment Tests; interference tests were performed during APXS and CONSERT operation. The *ROMAP* / RPC (ROSETTA Plasma

Consortium) combined test served for the cross-calibration of the *Lander* and *Orbiter* magnetometers.

In May 2014, the planned Pre-Delivery Calibration and Science Operations (PDCS) were executed on the Philae GRM. In September 2014, the planned Separation, Descent and Landing (SDL) and the First Science Sequence (FSS) tests, and in October 2014 additional tests in safe mode operations were executed on the *Philae* GRM, among others to imitate the operation of the *ROMAP* and *SESAME* instrument packages from separation from the *Lander* until the end of the first measurement sequence on the nucleus surface. All these tests proved the proper operation of the *DIM* and *SPM* instruments; however, an increased noise level during the operation of the Solar Array simulator was reported for *DIM*.

In the frame of the PDCS, measurements were performed with the instruments in October 2014 at a distance of 10 km from the comet nucleus. Measurement data were analyzed. Cross-calibration measurements with *ROMAP* and *RPC* were also performed. A High Voltage test of *ROMAP/SPM* was executed successfully in October 2014 before landing during the *Lander* Delivery Preparation phase of the mission.

Experts of MTA EK followed the developments of the SDL and FSS phase collocated with the other instrument teams between the 12<sup>th</sup> and 15<sup>th</sup> of November in 2014 in DLR, Cologne. Completeness and consistency of measurement data received were checked. Preliminary data evaluation also began. *DIM* was operated during *Philae*'s descent at 4 different altitudes above the comet surface, and at *Philae*'s final landing site, Abydos. During descent to the nominal landing site, *DIM* measured the impact of one rather big particle that probably had a size of a few millimeters. No impacts were detected at the final landing site which might be due to low cometary activity and/or due to shadowing from obstacles close to *Philae*.

From the magnetometer measurements performed on the *Orbiter* and the *Lander* in parallel, the scientists could reconstruct the time of touchdowns on the surface and the changes in the orientation and rotational periods of *Philae* during descent, the unintentional hopping on the surface and landing. After the first touchdown, measurements with *SPM* started and lasted for approximately 6 hours. After the landing the Sun direction could also be determined from *SPM* measurements. Results also imply that arrival at the final landing site was relatively slow due to the low gravitational forces on the surface of the comet.

### **Remaining work**

The evaluation of data obtained during descent and on the surface of the comet continues also in year 2015. Results will be published in peer-reviewed scientific journals.

After completing FSS, *Philae* entered into hibernation. As comet 67P/C-G gets closer to the Sun, there will be a chance that at better illumination conditions, the *Lander* will wake-up. Therefore, the planning for a possible Long Term Science phase will also continue.

### **Acknowledgement**

The Hungarian contribution to *DIM* and *SPM* was co-funded through PRODEX contracts and by the Government of Hungary through European Space Agency contracts No. 4000107211 and 4000107212 under the Plan for European Cooperating States (PECS).



# IMPROVEMENT OF THE METHODOLOGY USED FOR ESTIMATING THE PRIMARY LOOP ACTIVITY IN CASE OF A LOCA EVENT, PRELIMINARY ESTIMATION OF THE ENVIRONMENTAL DOSE

*András Keresztúri, Áron Brolly, István Panka, Tamás Pázmándi, István Trosztel, Péter Szántó*

## **Objective**

In the course of licensing the new 4,7 % enriched fuel, two high dose rates were obtained at the border of the radiological area by applying a very conservative assumption, namely that 100% of the fuels pins is non-hermetic in case of LOCA events. A new methodology avoiding the not necessary conservatism had to be elaborated for estimating the ratio of the activity released from the fuel pin. A further task was to recalculate the corresponding environmental dose rate in the vicinity of the NPP.

## **Methods**

The fuel pins of the whole core were classified according to the time dependent boundary conditions of the fuel behavior investigations which were taken from the previous sets of the LOCA multi hot channel calculations. After that, the FRPATRAN transient fuel behavior code was applied for these representative fuel pins. Beforehand, the FRAPTRAN code was modified by using the results of the previous blow-up measurement concerning both the classing mechanical properties and the damage conditions. The results were parametrized according to the initial linear heat rate and the burnup. By using this parametrization, the number of the failed fuel pins for a concrete core was determined. The activity transport in the containment and the release to the environment were calculated by using the CONTAIN thermo-hydraulic code and the TIBSO program.

## **Results**

It turned out that the assumption that 100% of the fuel pins fails is extremely conservative, namely less than 10% of them was damaged, in addition, most of them were of low burnup containing low level of activity. The effective dose was less than 1 mSv even during 50 year at 1 km distance from the NPP.

## **Remaining work**

There is no remaining work.

## **Related publication**

A. Keresztúri, Á Brolly, I Panka, T Pázmándi, I Trosztel, P Szántó, *Improvement of the Methodology Used for Estimating the Primary Loop Activity in Case of a LOCA Event*, Preliminary Estimation of the Environmental Dose Rate, MTA-EK-RAL-2014-715-03-M0, 2014, in Hungarian

# CHANGES IN DOSE RATE CAUSED BY THE PRIMARY CIRCUIT COMPONENTS DURING THE 15-MONTH OPERATING CYCLE

*Péter Szántó, Tamás Pázmándi*

## **Objective**

The aim of the study was to examine the impact of the new core on dose rates due to the components of the primary circuit. Knowing the dose rate it is possible to estimate the change of the employee's dose burden. We examined the expected change in the primary coolant activity concentration due to the introduction of the 15-month operating cycle. Dose rate changes caused by primary circuit components were estimated considering the change of activity in the primary circuit.

## **Methods**

We defined the average length of the 12-month operating cycle to be 7800 hour, while the average length of the 15-month operating cycle to 9960 hours. From the changes of activity concentrations we determined the changes of dose rate caused by devices in normal operation and 48 hours after outage. The evolving dose due to accumulated activity on the filter depends on the length of operating time of the resin. The change of dose rate is negligible.

## **Results**

Calculation for the upper part of the pressurizer showed 2-3% dose reduction. According to the model we used, based on conservative assumptions, 1-11% increase in dose rates in case of the other equipments were experienced. The results of the field measurement showed that the contribution of cesium does not exceed a few percent in the dose rate, therefore with the change to the 15 month operating cycle the change in dose rates will not exceed 1%. In case of normal operation, the change of dose rate caused by examined devices remained within  $\pm 2\%$  with the exception of the mixed-bed filter of VT-1 water treatment device.

## **Related publication**

T. Pázmándi, P. Szántó: *Changes in dose rate caused by the primary circuit equipments during the 15-month operating cycle*, report, EK-SVL-2014-799-01-01-02 (2014)



# DOSE CONSEQUENCES OF A SEVERE ACCIDENT

*Sándor Deme, Tamás Pázmándi, Péter Szántó*

## **Objective**

During the assessment of a new nuclear site, the effect of external radiological incidents on the operation of the new units should be analyzed. The most serious external radiological effect on the planned Paks-2 site is the severe accident of the Paks-1 NPP. The dose effect of a severe accident in Paks-1 NPP was assessed on the workers of the planned Paks-2 site.

## **Methods**

The dose consequences were calculated for three discharge scenarios:

- a. discharge from an open reactor,
- b. severe containment failure due to an earthquake
- c. discharge from the spent fuel pool.

Three meteorological cases were considered:

- 1) 1 m/s wind, dry weather, Pasquill F stability index (stable),
- 2) 2 m/s wind, dry weather, Pasquill D stability index (neutral stability),
- 3) 2 m/s wind, 20 mm/h precipitation, Pasquill D stability index (neutral stability).

The calculations were performed with the PC-COSYMA program.

## **Results**

Activity concentrations in the air and on the ground, external effective doses from the ground and the cloud, and committed effective dose from inhalation were calculated at 13 distances (100-1500 m) from the discharge point at 6 heights (0-50 m).

## **Remaining work**

This work is completed.

## **Related publication**

S. Deme, T. Pázmándi, P. Szántó: *Characterization of a heavy accidental radioactive pollution in the area of blocks 1-4 of the NPP Paks*, report, EK-SVL-2014-901-01-01-00 (2014)

## **IV. NUCLEAR SECURITY, NON PROLIFERATION**

# BURNUP MEASUREMENTS OF VVER- 440 FUEL ASSEMBLIES

*István Almási, Sándor Szabó, C. Tam Nguyen, Zoltán Hlavathy, László Lakosi*

## Objective

The aim was to continue the high resolution gamma spectrometric (HRGS) measurements started in previous years in order to support burnup calculations being performed at the Paks Nuclear Power Plant (NPP). Measurements are expected to indicate that the uncertainty of the burnup calculation is less than anticipated. Calculated burnup was aimed at to be verified by measurements according to the scheme in Fig. 1.

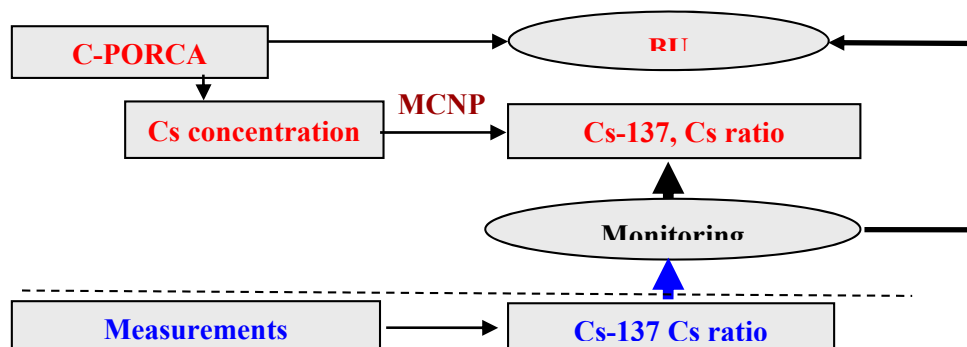


Figure 1: Scheme of verification

## Methods

As earlier, the measurements were carried out at Paks NPP by a 45 cm<sup>3</sup> HPGe detector placed behind a collimator built into the concrete wall of the service pit. Spent fuel assemblies were transported to measurement position and moved up and down as well as rotated under water by the refueling machine in front of the collimator hole. 3-3 assemblies in 4 groups of medium and high burnup and cooling times 1.8, 2.8, and 3.8 y were selected. Assemblies of the same position and history were taken for each group from sectors No. 1, 3, and 5 in the reactor core, so their burnup parameters were uniform, apart from turning angles of  $\pm 120^\circ$ . Spectra were acquired for 1200 s on average from 3 heights and 3-5 sides of the assemblies of an initial enrichment 3.82% (except for a 2.4% one) and of 1, 2, 3, and 4 y reactor operation times. <sup>137</sup>Cs activities and <sup>134</sup>Cs/<sup>137</sup>Cs activity ratios were measured and also calculated theoretically. Whereas the first quantity is strictly proportional to burnup, the Cs activity ratio is almost linearly related to it.

## Results

On the basis of the comparison made among measured results of the assemblies, the dispersion of Cs ratios varies between 1-3% in case of assembly groups of higher burnup, shorter cooling time. Measurement confidence is better than 2%. Theoretical burnup calculations are still going on. An example of the axial and azimuthal Cs ratio profiles of assemblies taken experimentally is shown in Fig. 2. The axial profile of an assembly of 40 MWd/kgU burnup and 3.8 y cooling time is seen at 3 heights as function of 3 turning angles of  $\pm 120^\circ$ , with an azimuthal profile at a single height for the coordinate point 2800 and 5 turning angles of  $60^\circ$  by  $60^\circ$ .

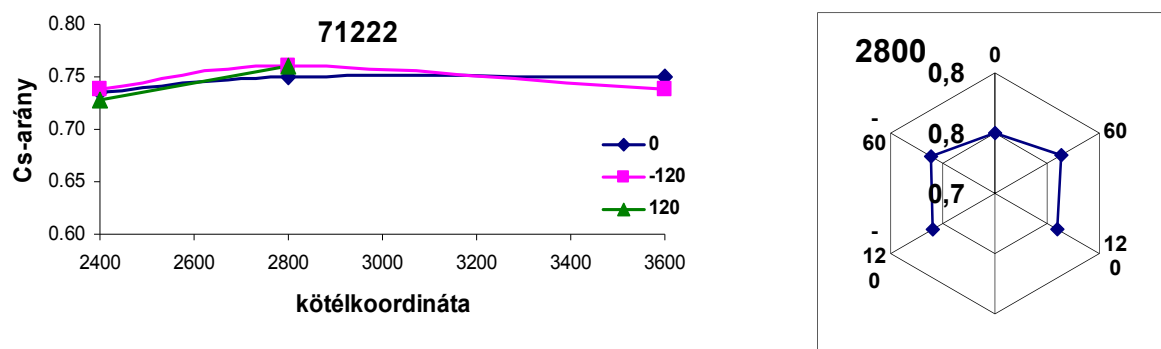


Figure 2: Measured Cs-ratio profile of an assembly of 40 MWd/kgU burnup and 3.8 y CT at 3 turning angles

## Remaining work

Further experiments are needed for improving the results. Burnup calculations are to be completed. Assemblies of even higher initial enrichments are to come to the NPP, giving additional motivation to the continuation of the measurements.

## Related publication

S. Szabó, I. Almási, et al., *Atomerőművi fűtőelemkazetták kiegészének mérése*, Report OAH/NBI-ABA-13/14-M, Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Oct. 2014.

# DEVELOPMENT OF A FAST, SELECTIVE, MORE SENSITIVE SAMPLE PREPARATION METHOD FOR IN-FIELD LIBS MEASUREMENTS FOR SAFEGUARDS PURPOSES

*Éva Kovács-Széles, István Almási*

## Objective

The aim of this work was to develop a fast, selective and sensitive sample preparation method for in-field analysis of liquid samples using Laser Induced Breakdown Spectroscopy (LIBS) technique. The method is simple and rapid enough, and should be applicable for even safeguards and nuclear forensic purposes. The sample preparation method is built on a pre-concentration step using different types of extraction chromatographic separation resins which can improve the selectivity and the sensitivity of the analysis. The method is applicable for analysis even for environmental and biological samples. Using the selectivity, it is possible to analyse only the important nuclides, e.g. uranium.

## Methods

For the selective sample preparation three different extraction chromatographic separation resins were used and tested firstly for selectivity by ICP-MS: TRU, UTEVA and CS resins. The first two are useful for separation of actinides (e.g. especially uranium or thorium) from different sample matrices. CS resin is useful for separation of cesium from environmental matrices. As a model matrix, the so-called "leechate" originated from different parts of a nuclear power plant (NPP). It contains different elements (e.g. B, K, Mg, Na) in higher amount and other elements in much lower concentration (Cu, Fe, Co, Cr, etc.). If there is an undeclared activity at the NPP, it is also possible to present uranium in these samples but in very low concentration. Another task was the construction of a suitable measurement cell for LIBS measurements using the liquid samples. Since the samples are usually hazardous, therefore a closed ablation cell is needed for safe measurements. To find the optimal conditions for LIBS analysis (focus, glass type, distances, fix of samples, etc.) is essential. Figure 1 shows one of the constructed cells.

## Results

The three types of resin were tested using different conditions and elution solutions (e.g. HNO<sub>3</sub>, HCl and NaOH, NH<sub>4</sub>NO<sub>3</sub>, respectively, in the case of CS resin) and model matrix. Selectivity of the resin and recovery for uranium and cesium was analysed. For uranium UTEVA was the most effective. For Cs: test of some other type of eluent is still necessary.



Figure 1: Closed ablation cell for LIBS analysis of hazardous materials using quartz window for UV detection

## Remaining work

This work was supported by the Hungarian Atomic Energy Authority in the frame of MMT projects. Continuation of the topic and further development for fast in-field sample preparation and analysis of liquid samples using a kit device is in progress.

## Related publication

É. Kovács-Széles, I. Almási: Gyors, szelektív és érzékenységnövelő mintaelőkészítő módszer kidolgozása terepen kivitelezhető, biztosítéki célú LIBS vizsgálatokhoz, OAH MMT research report, OAH-NBI-ABA-21/14-M (2014)

# SUMMARY AND FEASIBILITY STUDY OF THE NOVEL METHODS FOR FIELD AND LAB CHARACTERIZATION OF THE NUCLEAR MATERIALS

*Éva Kovács-Széles, Katalin Tálos*

## Objective

The first aim of this work was collecting the recent methods available in the literature for field and lab characterization of the nuclear matters with unknown origin and summarizing the potential of the latest devices of MTA EK, which can be used for determination of the missing or seized nuclear or other radioactive materials. After an overview of our techniques and other novel methods, an action plan and a lab procedure were processed in case of characterization of an unknown nuclear or other radioactive material. Furthermore, we made some recommendation for analytical plan of treating of terrorism action and for recovery the missing nuclear or other radioactive materials.

## Methods

Firstly, a collection of the devices for nuclear or other radioactive material characterization was carried out, which include the novel techniques from the literature and the instruments of MTA EK. These techniques are useful in case of confiscation, searching the missing sources or checking the location of a mass meeting. Our newest technique is Canberra GCW6023 HPGe gamma detector, which is well supplementing our instrument park of the nuclear forensics and permits of the age dating of the NU, DU and LEU samples.

Thereinafter, new results of the laboratory methods for characterization the nuclear or other radioactive material were summarized. For instance, the determination of  $^{233}\text{U}$  with AMS is a new method in the nuclear forensics. The AMS is also proper to determine the  $^{236}\text{U}$ . Determination of the  $^{236}\text{U}/^{238}\text{U}$  isotope ratio is an important factor for recognition of the geological information of the uranium ore

For preparing our nuclear or other radioactive material searching action plan, the *Nuclear Security Series No.2* published by International Atomic Energy Agency was the basic literature. After considering the Hungarian regulation and laws of the information pathway and the potential materials characterization methods, our own action plan was prepared, which can be a foundation or recommendation for the Hungarian national response plan. In addition, our laboratory proceeding for handling the seized and found nuclear and other radioactive material was formulated.

## Results

During the study, the novel literature and our sources of the field and lab methods for detection and characterization of the nuclear and other radioactive materials were reviewed. On Figure 1., 2. and 3. some examples for the detection devices can be seen, which can be used for detection and identification of a potential missing or seized radioactive or nuclear material. After summarizing the literature, the laws and the international recommendations, the analytical action plan of the Nuclear Forensic Laboratory for characterization and origin assessment of the materials with unknown origin was created.



Figure 1: Thermo RIIDEye X-H

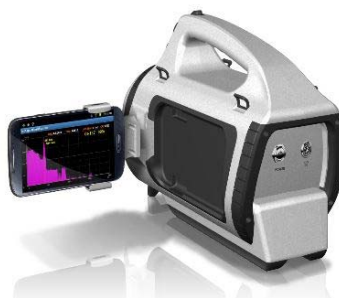


Figure 2: NC SAM 9



Figure 3: BNC Pager 1703GN

## Remaining work

Following the experiences during the study preparation of action plans for detection of orphan sources and lost nuclear materials within a site and investigation of a radiological crime scene in Hungary is in progress.

## Related publication

É. Kovács-Széles, K. Tálos: *A nukleáris anyagok helyszíni és laboratóriumi karakterizálására alkalmas legújabb módszerek felmérése és gyakorlati megvalósíthatóságának vizsgálata*, OAH MMT research report, OAH-NBI-ABA-11/14-M (2014)

# DEVELOPMENT OF A NUCLEAR FORENSIC METHOD FOR CHARACTERIZATION AND ORIGIN ASSESSMENT OF SPENT FUEL

*Éva Kovács-Széles, Nguyen Cong Tam, László Lakosi*

## Objective

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard to the public and the environment as well as the security risks associated with nuclear and other radioactive material out of regulatory control. Nuclear forensics is the tool for origin assessment of nuclear materials originated from a confiscation. Through nuclear forensic analysis, information on the history and on the potential origin of intercepted nuclear material can be obtained by investigating the characteristic parameters of such material. However, illicit trafficking of these materials and therefore most of the characterization method in nuclear forensics focuses on fresh fuel or uranium ore concentrates while spent fuel would also be interesting and a real risk in smuggling even the possibility is low.

## Methods

Isotope correlations can be obtained as isotopic ratios versus a surrogate for exposure time in the reactors (e.g. burn-up, build-up of Pu, etc.). Using such correlations it is possible to identify differences between reactors or classes of reactors. In this work the burn-up was used for creation of classes from reactors. Basic assumption is that neutron fluence distribution in the reactor zone is different in every reactor. Therefore, using burn-up and various isotope correlations as well as initial enrichment as parameters of the nuclear fuel, characteristic data and distinct classes can be obtained from the data of reactors.

## Results

Ratio of U-234/Total U vs. burn-up of a hypothetically seized sample can be seen in Figure 1. The different coloured points indicate the distinct groups of different reactors (origin). It can be seen that data points result in most of the cases distinct groups or classes among the reactors. Moreover, in the case of one of the reactors (so called Daphnis) 2 individual groups can be found within the reactor. Considering the fitting of the data points of the hypothetically seized samples it is seen that they are consistent with the data points of one group of Daphnis reactor (Pin1). Using our method and the calculated parameter, the origin of hypothetically seized spent fuel can be identified. However, it is important to note that for such kind of investigations the knowledge of reactor operation and spent fuel characteristics is also important together with well-used statistical evaluations.

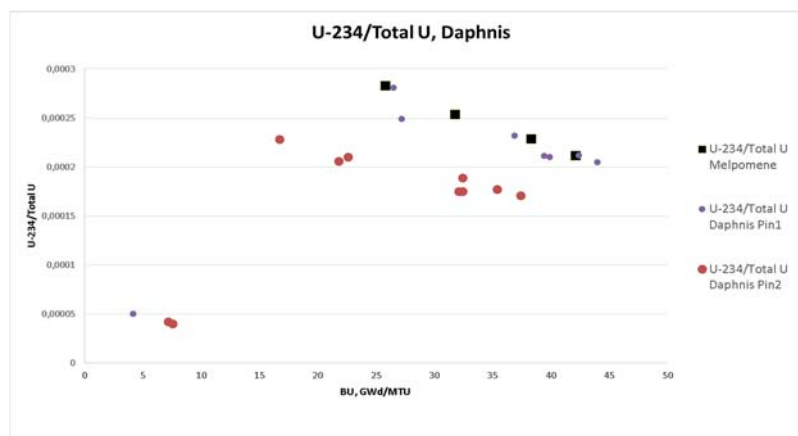


Figure 1: The ratio of U-234/Total U vs. burn-up of a hypothetically seized sample and its identification

## Remaining work

This work was supported by the Hungarian Atomic Energy Authority in the frame of MMT project. At the same time it was a part of a virtual table top exercise for how to create and use a National Nuclear Forensic Library. Further statistical evaluation of the database of spent fuel samples available is in progress. Connecting to the topic, the second table top exercise has been prepared for 2015.

## Related publications

- [1] I. Almási: *Nukleáris törvényszéki analitikai módszer kidolgozása az atomerőműből származó kiegészített nukleáris anyagokra, azok karakterizálásához*, OAH MMT research report, OAH-NBI-ABA-12/14-M (2014)
- [2] Éva Kovács-Széles, Sándor Szabó, Tam Cong Nguyen, *The Hungarian Experience in the Galaxy Serpent Tabletop Exercise on National Nuclear Forensics Libraries*, Journal of Nuclear Materials Management, Volume XLII, Number 4, 2014, 65-70 pp.

# SAFEGUARDS MEASUREMENTS AT PAKS NPP

*István Almási, Zoltán Hlavathy, Zsuzsanna Kovács*

## Objective

The aim was to verify the enrichment of freshly arrived fuel as a routine method developed earlier, before they are loaded into the reactor core.

Spent Fuel Attribute Tester (SFAT) developed earlier was used to perform attribute testing of assemblies and other objects stored in the spent fuel storage ponds.

## Methods

Fresh fuel measurements were carried out in the fresh fuel storage at Paks NPP by a 95 cm<sup>3</sup> HPGe (high purity germanium) detector (for outer fuel pins in an assembly), placed to the detector holder rack at the half-height of the assembly, and a 20 mm<sup>3</sup> CZT (Cadmium-Zinc-Telluride) detector (for inner pins), placed into the assembly central hole. Enrichment verification relied on the measurement of the 186 keV energy gamma-rays of U-235, as compared to reference assemblies of 1.6 and 2.4% enrichment.

SFAT comprises a 500 mm<sup>3</sup> CZT detector with an air collimator and a lead shielding. The bottom of the collimator is connected to the head of the assembly, which the CZT detector is positioned against. The air collimator consists of eight 1 m long modules, forming a shield against gamma-rays from neighbouring assemblies. The 662 keV energy <sup>137</sup>Cs peak was detected from the irradiated fuel with 1 - 15 years cooling time, whereas <sup>134</sup>Cs peaks (605, 795 keV) were detected from 1- 5 years cooling time assemblies. The method can substitute the Cherenkov viewing device under adverse circumstances (bad water transparency, long cooling time, etc.)

## Results

Altogether 63 fresh profiled assemblies (about 10% of the received ones) enriched to 4.2 and 4.7% (on average) were verified. ("Profiled" assembly contains fuel pins of different enrichments). The enrichment of inspected assemblies agreed with declared one within the uncertainty limit. Measured data were checked by MCNP simulation, taking into account the declared pin-composition of the profiled assemblies. Some assemblies were checked on all their 6 sides. Three examples are shown in Fig.1. Red profiles are those of two assemblies, grey ones represent averages, whereas dashed-dotted lines correspond to  $\pm 2$  STD (standard deviations) from the averages. The asymmetry of one assembly (profile in blue) exceeded 2 STDs. We suggested its control by another method.

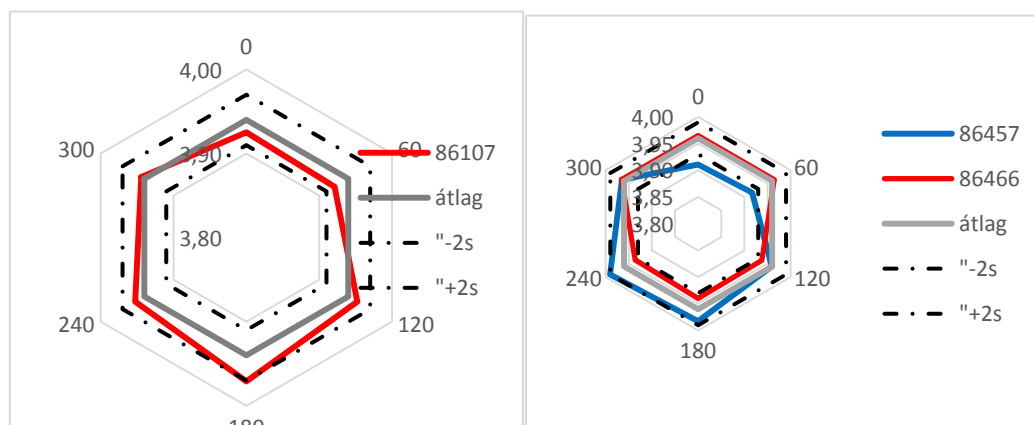


Figure 1: Results of 3 assemblies measured on their 6 sides (values in peaks correspond to those measured on sides)

Four measurement campaigns were performed by the SFAT, one of them in cooperation with the Euratom inspector. All the four spent fuel ponds were checked for 29 assemblies and 8 canisters in them, the latter filled with nuclear material from damaged assemblies, except for one canister that was declared empty.

The <sup>134</sup>Cs (605, 795 keV) peaks and the 662 keV energy <sup>137</sup>Cs peak were easily identified in the gamma spectra, except for the empty canister. Consequently, all the other tested objects were containing spent nuclear fuel.

## Remaining work

We have long term contracts for routine measurements with Paks NPP.

## Related publications

[1] I. Almási, Z. Hlavathy, Zs. Kovács, *Mérések a friss üzemanyag-tárolókban és SFAT mérések a pihentető medencékben 2013- és 2014-ben*. Report under contract No. 4000022723 EK-G 1087/2013-31-2 concluded with Paks NPP, Budapest, 2014.

[2] I. Almási, Z. Hlavathy, Zs. Kovács, *Mérések a friss üzemanyag-tárolókban és SFAT mérések a pihentető medencékben 2013- és 2014-ben*. Report under contract No. 4000022723 EK-G 1087/2013-32-2 concluded with Paks NPP, Budapest, 2014.



## **V. RENEWABLES AND FOSSIL ENERGY PRODUCTION**

# WATER OXIDATION – INITIAL STEPS

József S. Pap, Mounir Chamam,  
Dávid F. Srankó, Zsolt G. Kerner

## Objective

We have framed water oxidation catalysis as a new, experimental research directive in 2014. The instant objective was to explore adaptable ways to efficient catalysis. The reaction itself:  $2\text{H}_2\text{O}(\text{f}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$  ( $E^\circ = 1.23 \text{ V}$ ) is a great challenge in catalysis and subject to intense research due to its importance in renewable water splitting to  $\text{H}_2$  and  $\text{O}_2$ . Our long term objective is to find catalysts that can make part of a complex (photo)catalytic water splitting system. Three directions were appointed: (1) Ru-diimine complexes, a) catalytic properties in homogeneous solution, b) anchoring options on supports, c) design and synthesis of photosensitizers, (2) design and synthesis of ligands for Ru-based metal organic frameworks (MOFs) to test in water oxidation, (3) synthesis and characterization of Cu-complexes for catalysis and looking into their anchoring options on electrode surfaces a) with diimine ligands, b) with branched peptides.

## Methods

Syntheses of the diimine and other imine heterocyclic ligands were carried out by standard condensation or C-C coupling reactions, initial characterization was done by MS and FTIR. Surface-anchored Ru-diimines were investigated by XPS, XRD and TEM [1]. Peptides were synthesized by improved solid phase method [3]. Several spectroscopic techniques (UV/VIS, CD, EPR), ESI-MS and electrochemistry were applied to characterize the Cu-peptide catalysts. Catalytic tests were run by cyclic voltammetry or controlled potential electrolysis, dioxygen evolution was monitored by a fluorescent probe.

## Results

(1) A NiFe-LDH (layered double hydroxide) was modified by molecular photosensitizer. The LDH was chosen because it is built of inexpensive ingredients, has layered structure that can accommodate molecules either by surface adsorption or (more desirably) by intercalation and both metals are redox active. Moreover, the NiFe-LDH acts not only as inert support, but it has catalytic activity. Our initial study demonstrated that this substance is a UV light responsive electrocatalyst in water oxidation when adsorbed on ITO anode surface [1]. Also, a novel Ru(II)-diimine photosensitizer was successfully included into a NiFe-LDH-terephthalate-Ru(II)-diimine assembly and will be tested by visible light activation.

(2) Synthesis of new ligands for Ru-MOFs has been ceased at an early stage (only general ligand precursors have been synthesized) due to the lack of external funding.

(3) We reported branched peptides based on the L-2,3-diaminopropionic acid (dap) junction unit [3] that form stable 1:1 complexes with Cu(II) [2,3]. These new complexes have been fully characterized in solution, among others, by the simulation of their pH-dependent EPR signals. Cu-complexes may be efficient electrocatalysts for water oxidation at elevated pH, if they are sufficiently stabilized in the Cu(III) form by the ligand environment and/or undergo proton-coupled-electron-transfer (PCET) reactions. Cu-complexes with two ligands were subject to detailed electrochemical characterization: H-Gly-Dap(H-Gly)-Gly-NH<sub>2</sub> (3G) and H-Gly-Dap(H-Gly)-His-NH<sub>2</sub> (2GH). The latter contains one extra N-terminal 4-ylmethylimidazole moiety that participates in Cu(II) binding. Pourbaix (potential vs. pH) diagrams of the Cu-3G and Cu-2GH systems were taken in the basic pH region and formal potentials of the PCET reactions were determined. Among electrocatalytic conditions at pH 11 the two complexes differ in their coordination environment and stability. Yet, pH-sensitive Cu(III)/Cu(II) electrochemical responses occur, leading to efficient WOC in both cases. The branching, in addition to the enhanced stability of the complexes in comparison with linear peptides, can be used as a linker to build heterogenized catalytic centers, or building blocks for metallo-dendrimers.

## Remaining work

In the upcoming year two fields will be in focus: a) adsorption/intercalation of Ru(II)-diimine photosensitizers by LDHs and activation of this assembly by visible light, b) anchoring molecular catalysts on ITO electrode surface to get modified anodes for electrocatalytic water oxidation.

## Related publications

- [1] D. F. Srankó, Z. E. Horváth, D. Szülek, Z. Kerner, J. S. Pap: *Synthesis and characterization of novel Ru(II)-diimine complexes for combination of layered double hydroxides*, 12<sup>th</sup> Pannonian Symposium on Catalysis (2014)
- [2] Ł. Szyrwił, M. Shimura, J. Shirataki, J. S. Pap, Ł. Szczuľkowski, B. Setner, Z. Szewczuk, W. Malinka, L. Chavattel, R. Łobinski: *The Cu(II) and Ni(II) binding properties of de novo branched peptides based on 2,3-diaminopropionic acid and their in vitro metal ions cellular trafficking features*, J. Biol. Inorg. Chem. **19** (Suppl. 2), S777 (2014)
- [3] Ł. Szyrwił, Ł. Szczuľkowski, J. S. Pap, B. Setner, Z. Szewczuk, Z. Malinka: *The Cu<sup>2+</sup> Binding Properties of Branched Peptides Based on L-2,3-Diaminopropionic Acid*, Inorg. Chem. **53**, 7951-9 (2014).

# CHEMICAL ENERGY STORAGE TECHNOLOGIES USED FOR INTEGRATION OF INTERMITTENT PRODUCTION, IN CONSIDERATION OF THE HUNGARIAN ELECTRICITY MARKET

*Endre Börcsök, Bálint Hartmann, Szabina Török, Veronika Oláhné Groma, Sándor József Papp*

## Objective

International experiences have clearly demonstrated the previous presumption that integration of intermittent renewable energy production can largely be supported by the use of energy storage. Since the construction of a pumped hydro plant in Hungary does not seem likely in the near future, other technologies, like power-to-gas solutions should also be examined. The objective of the research was to present an overview of boundary conditions (obligatory electricity purchase tariff, penalty tariff, balancing energy tariffs and technical parameters), and determine scenarios in which the cooperation of an intermittent renewable-based generator and a power-to-gas storage unit would result in lower operation costs, compared to the independent operation of the power plant.

## Methods

During our work it was assumed that load-following power plants are running solely on intermittent renewable sources. Processing of solar and wind electricity generation data was performed using a 15-minute temporal resolution of year 2013. Based on the utilization factor, the installed necessary wind and solar power were chosen as 7400 MW and 12 250 MW, respectively. As expected, due to its stochastic nature, wind power does not show correlation with the power curve, and photovoltaics – being considered as better matching consumption needs – show small ( $r=0.25$ ) correlation. Direct comparison of production data also allowed to examine the ideal proportion of wind and solar power as a linear optimization problem; according to our calculations installed capacity of wind (4990 MW) should be approximately 25% higher than that of solar photovoltaics (3960 MW). A possible option to improve the low time coincidences of generation and consumption need the use of energy storage.

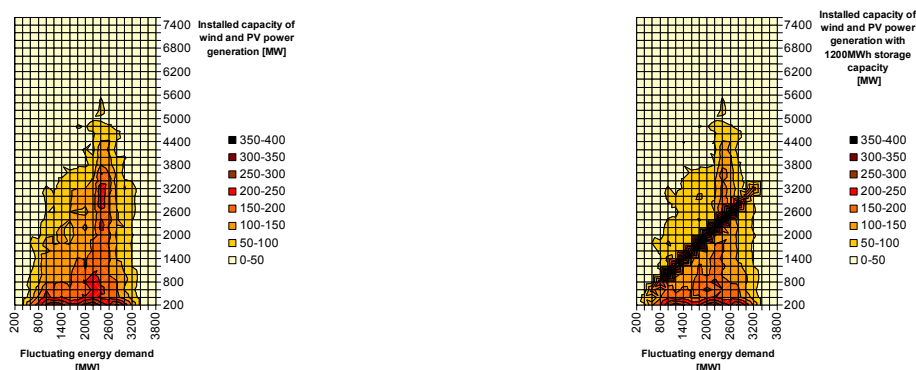


Figure 1: Frequency of the coincidence of demand and intermittent power supply

Two different storage options were examined, Li-ion batteries and hydrogen storage. Regarding storage, the following assumptions were made: only renewable-based energy is used for charging, the proportion of stored energy must not exceed 50% during any given hour and the storage is discharged once a day. Detailed technological and economical parameters of both Li-ion batteries and hydrogen storage were collected, based on literature review and previous work. Potential income of these plants was calculated using two different tariff structure; first the current prices of obligatory electricity take-off were used, then spot pricing was implemented. A multiplier of the spot prices was used in all cases when spot prices were above the average, thus ensuring that the estimated income of the plant was equal for both tariff structures.

## Results

Preliminary results have shown that the joint concept of the application of dynamic pricing and the use of energy storage is able to support the integration of intermittent renewable generation, without increasing the total amount of subsidies. Similarly, power-to-gas solutions are only competent today if the generated fuel is used by the transportation sector.

## Remaining work

Detailed economical comparison of the two storage technology options has to be performed.

## Related publications

- [1] B. Hartmann, E. Börcsök, V. Oláhné Groma, J. Osán, A. Talamon, Sz. Török, M. Alföldy-Boruss: *Multi-criteria Revision of the Hungarian Renewable Energy Utilization Action Plan – Focusing on the Aspect of Economy, Renewable Energy – submitted* (RENE-D-15-00017)
- [2] E. Börcsök, B. Hartmann, J. Osán and Sz. Török: *Economic Evaluation of Energy Storage Solutions Cooperating with Intermittent Renewable Generation – Manuscript in preparation* [in Hungarian]

# NUMERICAL SIMULATION OF AEROSOL DRUG DELIVERY TO THE HUMAN AIRWAYS

Árpád Farkas, Imre Balásházy, Ágnes Jókay, Péter Fűri

## Objective

The primary objective of the work was to develop numerical models of aerosol drug transport and deposition within the airways of patients suffering from obstructive pulmonary diseases. Further aim was to work out algorithms that can assist pulmonologists in the selection of appropriate aerosol drugs and in the optimization of drug intake.

## Methods

Models and software have been developed to quantify the deposition distribution of the most frequently used aerosol drugs currently available in the domestic market applied for the treatment of asthma. This task basically implied the integration of the so called asthma factors into the Stochastic Lung Model to make it applicable to healthy subjects as well as patients with a broad variety of pulmonary diseases. The new model has been validated against experimental data. The validated code has been applied to a group of volunteers. Spirometry measurements have been performed on these volunteers and then the corresponding spirometry data were measured also through the selected inhalation devices which have different resistances.

## Results

Relationships between breathing parameters measured during diagnostic spirometry and those characterising breathing during drug administration through inhalers have been derived. Based on the respiratory functional data, airway deposition distributions of the three most frequently used aerosol drugs have been computed for each volunteer (Fig. 1.). Our results demonstrate that the regional deposition fractions of each selected aerosol drug was patient specific, which indicates the necessity for and opens the possibility of simulation assisted customized drug selection. The appropriateness of the different drugs and breathing modes proved to be quite sensitive also to the definition of the target area. Our results highlight the potential of an individualised and optimised aerosol drug delivery and treatment of lung diseases in the future.

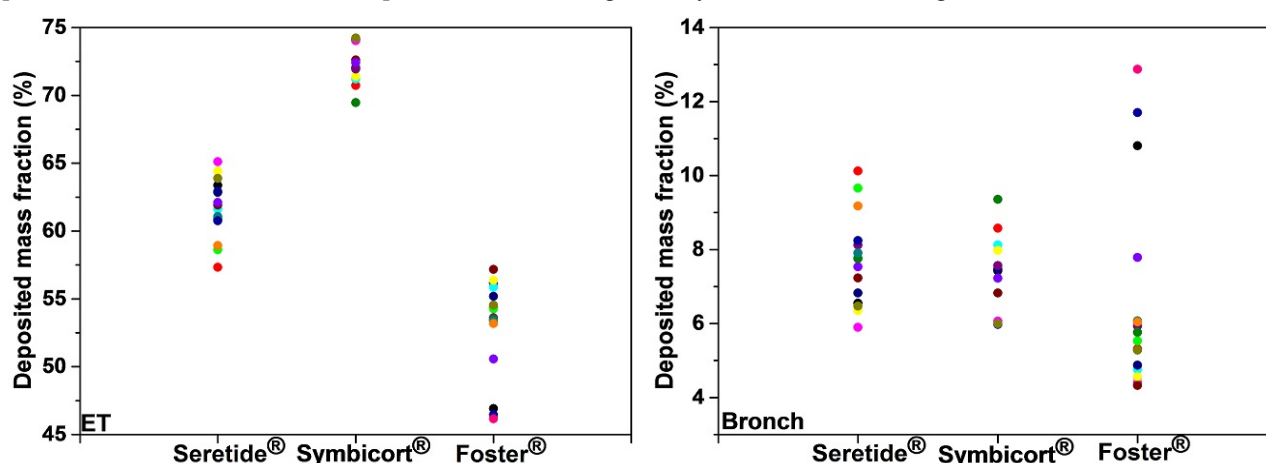


Figure 1: Extrathoracic (left panel) and bronchial (right panel) deposition fractions of three selected aerosol drugs (2 powders, 1 spray) in asthmatic patients

## Remaining work

Inclusion of COPD factors into the Stochastic Lung Model will be performed. Aerosol deposition computations for COPD patients are foreseen for the next period. Comparison of simulated and measured deposition distributions and optimisation of drug delivery will also be performed.

## Related publications

- [1] Á. Farkas, I. Balásházy, Á. Jókay and P. Fűri: *Simulation of Airway Deposition and Clearance of Aerosol Drugs*, Book of Abstracts PP18-008, International Aerosol Conference, Busan (2014).
- [2] Á. Jókay, Á. Farkas, I. Balásházy, P. Fűri, A. Horváth and V. Müller: *Numerical modelling of airway deposition of inhalation corticosteroid - long acting  $\beta_2$  agonist (ICS-LABA) combined aerosol drugs commonly used in asthma therapy*, *Medicina Thoracalis* **68**, 46-57 (2015), In Hungarian.

# MULTI-CRITERIA EVALUATION OF RENEWABLE ENERGY UTILIZATION IN ELECTRICITY, HEAT GENERATION AND TRANSPORTATION SECTORS

*Endre Börcsök, Veronika Oláhné Groma, Bálint Hartmann, János Osán, Szabina Török*

## Objective

In 2012 the Hungarian Government decided to revise the country's National Renewable Action Plan, mostly due to the experienced changes of the economical environment and the continuously decreasing cost of renewable energy technologies. Due to significant changes of the economy on national and global level, total primary energy needs are estimated to reach only 760 PJ in 2020 in contrast to the previously anticipated 823 PJ. Approximately half of this value will be consumed in the heat energy sector, while electricity generation and transportation sectors will account for 25-25%, each. To reach the targeted 14.65% share in total energy consumption, 116.5 PJ should be provided from renewable sources. For the transportation sector the minimal required share (10%) equals to 19 PJ. The revision of the previous scenarios (published in the "Energy Strategy 2030") was aided by multi-criteria decision analysis (MCDA) ranking of all potential renewable technologies and their respective fuels on few economic and social (environment, climate, job creation and innovation) criteria.

## Methods

The methodology, applied by the authors, consists of three steps. The first step focuses on the estimation of sustainable potential on the individual county level. Bioenergy and geothermal energy are the only sources with high potential, existing in most regions of Hungary. The total ranking of renewable energy potentials are shown in Table 1.

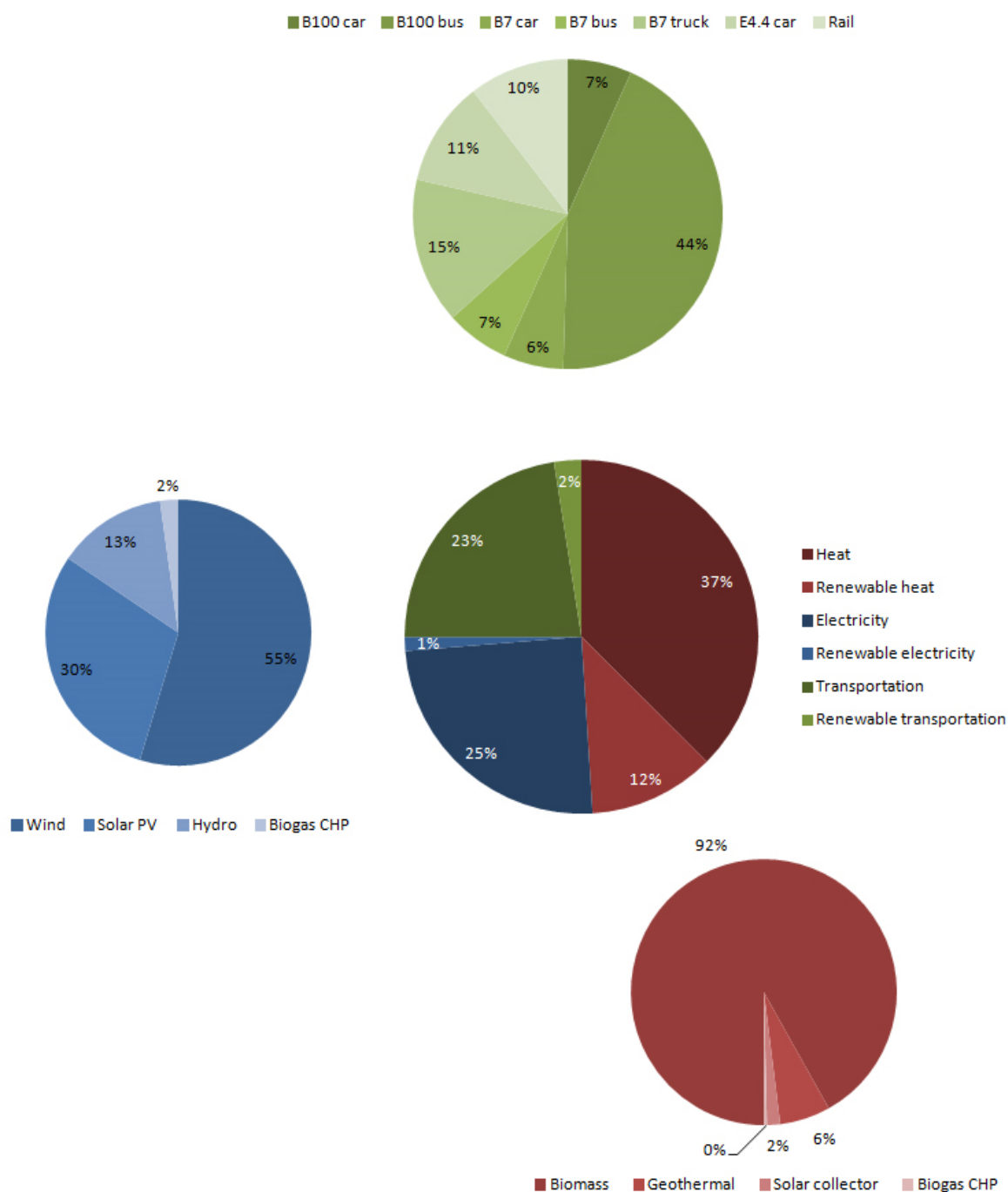
Energy source	Category				
	#1	#2	#3	#4	#5
Wind	1	3	6	1	9
Solar photovoltaic	1	5	9	4	1
Solid biomass	2	5	3	5	5
Biodiesel	4	6	3	5	2
Bioethanol	4	6	3	6	1
Bioenergy by-products	4	6	3	6	1
Geothermal heating plant	6	10	0	0	4
Geothermal heat pumps	6	10	0	0	4

*Table 1. Distribution of renewable energy potential among the 20 administrative units of Hungary, #1=best, #5=worst*

The second step is to compile all technologies that might be suitable for energy generation or transportation, using renewable fuels based on end-user demand. For these technologies, specific investment, operation and maintenance costs were calculated and future prices trends were also assessed. When examining the electricity and heating/cooling sectors, regional potentials (wind, hydro, solar, forestry and agricultural by-products, municipal waste, geothermal energy) and demands (heat demand of family houses, apartment houses and blocks of flats) were assessed. Regional renewable quotas and shares were calculated by an optimization algorithm. The optimization of the transportation sector was handled independently from electricity and heating/cooling sectors. The target of the transportation sector (at least 10 E/E%) is reached by increasing the blending of renewable fuels (up to technological limits) and by changing the fuel of large fleets (e.g. public transport). In final step the sectorial energy use was determined by performing MCDA optimization for each additional 1 GJ. In every iteration cycle both energy needs and potentials are re-evaluated, and technologies are ranked.

## Results

The scenario resulting from the optimization highlights that by 2020 renewable energy in Hungary should still mostly be produced from biomass. The dominance of biomass in the heating sector is playing a key role in this (Figure 1). In the transportation sector, biofuels should account for 90% of total renewable use.



**Figure 1:** (centre) Share of renewable energy sources in the Hungarian energy mix in 2020 (total consumption: 760 PJ); (top) detailed share of renewable energy in transportation sector (total share 2%); (left) detailed share of renewable energy in electricity generation (total share 1%); (bottom) detailed share of renewable energy in heat generation (total share 12%)

### Related publications

- [1] E. Börcsök, B. Hartmann, I. Kitinger, V. Oláhné Groma, J. Osán, Á Szabó, A. Talamon, Á. Török, Sz. Török: *Comparison of renewable energy generation technologies based on economical and environmental criteria*, Report to the Ministry of National Development, 2014. [in Hungarian]
- [2] B. Hartmann, E. Börcsök, V. Oláhné Groma, J. Osán, A. Talamon, Sz. Török, M. Alföldy-Boruss: *Multi-criteria revision of the Hungarian renewable energy utilization action plan - focusing on the aspect of economy*. Renewable Energy, 2015 (submitted)

## **VI. ENERGY SAVING AND ENVIRONMENT STUDIES**



# HYDROXYL RADICAL ( $\cdot\text{OH}$ ) REACTION WITH FENURON

Viktória Mile, Ildikó Harsányi

## Objective

The aim of this project was to support theoretically the experimentalists in interpreting the elementary steps of hydroxyl radical reaction with fenuron, investigated using radiation chemical methods and observation of the intermediates and final products. The main reaction is  $\cdot\text{OH}$  addition to the ring resulting in hydroxycyclohexadienyl radical. The electron donating urea side chain is expected to direct  $\cdot\text{OH}$  to ortho- and para-positions, but three ring monohydroxylated products were observed, so meta-addition should also occur. Ipso-addition is probably of low importance due to thermodynamic and steric reasons. These reactions were studied by density functional theory calculations. The main question is: whether the calculated energetics of reactions support the reaction mechanism suggested based on the experimental results.

## Methods

In order to study reaction  $\cdot\text{OH}$  with fenuron we used density functional theory. Optimization and frequency calculations were carried out at B3LYP level using 6-311G++(d,p) basis set by ORCA software.

## Results

In order to determine the ground state structure of fenuron, an internal twisting of dimetilurea group was investigated. Planar structure was obtained for ground state. The  $\cdot\text{OH}$  radical addition to the ring has been modelled with a relaxed surface scan. Figure 1.a shows the result of this calculation in case of ipso addition. The geometries at the energy minimum and maximum correspond to addition complex and transition state, respectively. The possible products (the addition complexes) are shown in Figure 1.b. After optimization of these structures frequency calculations have been executed.

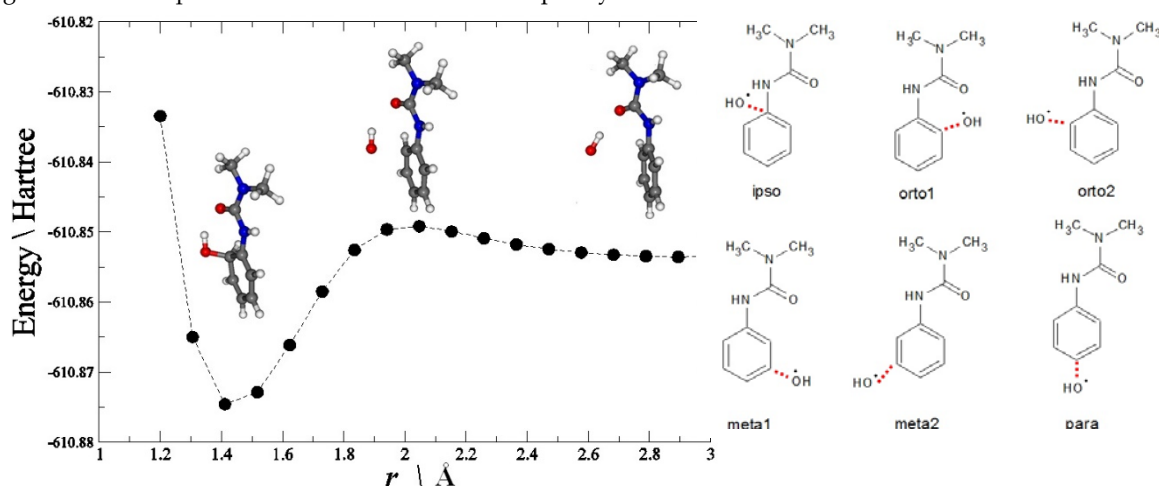


Figure 1: a (left): Relaxed surface scan for the  $\cdot\text{OH}$  addition to the ring ( $r$  is  $\text{C}_{\text{ring}} \cdots \cdot\text{OH}$  distance); b (right): the possible addition complexes

Reaction energies and activation energies of the addition reaction are given in Table 1. The values of the reaction energies support the mechanism suggested based on the experimental results. Ortho- and para-addition of  $\cdot\text{OH}$  to the ring are energetically favourable, while ipso and meta addition are not favourable. Considering both activation energy and reaction energy the most favoured position of addition is ortho2.

Table 1: Reaction energies and activation energies of  $\cdot\text{OH}$  addition to fenuron

	ipso	ortho1	ortho2	meta1	meta2	para
reaction energies \ kJ/mol	-55.061	-64.664	-68.039	-44.622	-45.522	-54.367
activation energies \ kJ/mol	11.624	-3.036	-15.057	4.789	1.205	-5.398

## Remaining work

Ortho-addition has to be studied in more details to find out the reason of negative activation energy. Radiation chemical measurements of fenuron, monuron and diuron molecules have been carried out in our laboratory. Quantum chemical calculations of the reaction between these molecules and  $\cdot\text{OH}$  radicals are still in progress. Synchronization and constant comparisons of theory and experiments are necessary in order to support experimental work. Theoretical calculations, for example kinetics calculation, can help the interpretation of the results of LINAC measurement.

## Related publication

K. Kovács, V. Mile, T. Csay, E. Takács, L. Wojnárovits: *Hydroxyl radical induced degradation of Fenuron*, Environmental Science and Pollution Research **21** 12693-12700 (2014)

# MODELING THE TRANSPORT OF RADIONUCLIDES IN SURFACE WATER

*Barbara Brockhauser, Emese Homolya, Tamás Pázmándi, Péter Szántó, Péter Zagyvai*

## Objective

Discharges of nuclear power plants by the riverside into rivers can raise many environmental issues. To determine the environmental effects of a possible radioactive emission, the radionuclide transport in surface water needs to be considered. Different methods are used in the international practice for the modeling of radionuclide transport in water. In order to determine radiation burden in the vicinity of an emission source, modeling the transport of radioactive material in the environment is crucial. Our objective is to create a transport model for radionuclides in rivers. The connection with sediment also plays an important role in the calculation of activity concentrations. The sorption processes (adsorption, desorption) that occur mainly on suspended sediment, increase or decrease activity concentrations in both water and sediment and need to be taken into account.

## Methods

A basic and not yet validated model has been created to calculate activity concentration from water and sediment, for different pathways. The model calculates values caused by accidental releases. One of the main factors is the shape of the riverbed which can be rectangular, trapezoid or parabolic in our model. The mechanism for the sorption effects are described with a  $K_d$  [l/kg] distribution coefficient that describes the exchange processes of radionuclides between the dissolved and the sediment phase.

## Results

Analyses were carried out for isotope I-131 that has a half-life of 8.02 days, with a release of  $10^9$  Bq. The calculations were made for instantaneous release from a shoreside point source. Calculations were made for three distances: 5 km, 10 km and 50 km. In the case of the trapezoid riverbed, concentrations were calculated assuming different side slope values ( $r$ ). Activity concentrations for the three distances are showed in Figure 1 for different channel types. Results suggest that the use of the parabolic type results in 50% less concentration at the shore side for all the three distances than the use of the rectangle type. When taking meanders into account, the concentration distribution in the transverse direction becomes smoother. Maximum concentration values at the shore side (Fig. 2) show a significant difference.

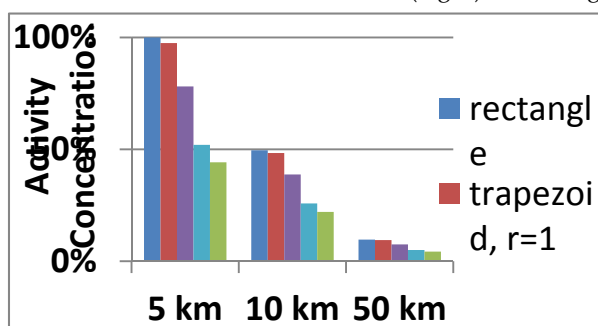


Figure 1: The activity concentration for different channel types and for different distances from the release

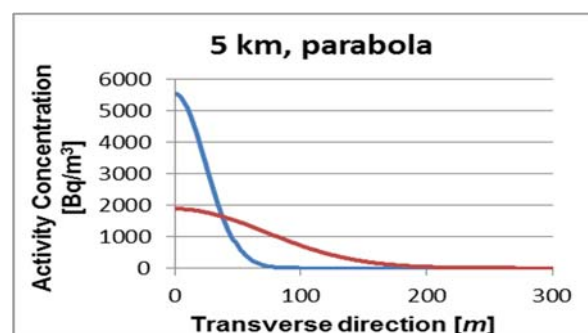


Figure 2: The lateral distribution of the activity concentration with (red) and without (blue) meanders

## Remaining work

The remaining work is to complete the model with more accurate modules and to make sensitivity analyses with the new modules. Future field studies are considered for more accurate habit data about the people living near the power plant and for determination of better dose conversions values and dose calculations.

## Related publications

- [1] B. Brockhauser, E. Homolya, T. Pázmándi, P. Szántó, S. Deme, P. Zagyvai: *Modeling radionuclide transport in major rivers*, 4<sup>th</sup> European IRPA Congress, Geneva, Switzerland (2014)
- [2] B. Brockhauser, T. Pázmándi, L. Hoffmann, E. Homolya, P. Szántó: *Transport of radionuclides in surface water*, MTA EK report, in Hungarian (2014)

# FEASIBILITY STUDY ON MATERIALS IN ENERGY STORAGE

*Ildikó Harsányi, Viktória Mile*

## **Objective**

The objective of this project was to find answerable scientific questions in the field of energy storage. The first question was to detect changes of structure and electrochemical behavior of lithium-lithium-oxide/-peroxide/-hydroxide layers with the thickness by experimental and computational methods.

## **Methods**

The goal was to prepare samples of metal lithium with different layers on top. The thickness and structure of the layer should have been examined by XPS and maybe with SEM methods. Additionally, conductivity of the layers should have been measured by impedance spectroscopy. In case of sensible results, theoretical modelling was planned to be applied to support, explain or just reproduce the experimental results.

Density functional theory calculations have been carried out to see how far we can get with local knowledge; results for the energy and geometry optimization for lithium ions and smaller molecules published in the literature have been reproduced well, without new materials this direction of research stopped here.

## **Results**

Unfortunately, the project failed before preparing samples. Samples were planned to prepare by exposing slices of lithium ribbons in water and/or oxygen for shorter and longer times. The samples should have been kept in Ar atmosphere, which is reliable for a few hours in sample holders, hence measurements should have had to be synchronized with sample preparing. This aspect seemed to be doable, the XPS measurements have been planned as well in the catalysis lab, where it would have been possible to mime Ar atmosphere. The measurements have been postponed for a few months.

The main conclusion of this question-finding research project was written in the report last year: the field lithium ion batteries are examined a lot in bigger institutes for long time, samples are not easy to deal with and locally the knowledge is not enough concentrated yet to start relevant research. The direction suggested a year ago as well in the field of renewable energy – staying beside energy storage – was fuel cells. Research groups in Hungary are working with different research aspects of fuel cells, finding connection with them seems to be a promising idea. We are in contact with András Tompos and his research group and started learning theoretical methods specialized for the field like the COMSOL program has a special package for modelling fuel cells.

## **Remaining work**

The experimental part of the project was postponed, and in the meantime parallel discussions drove to the decision that we should focus more on fuel cells. The experimental skills would follow the hydrogen/water transport, fluidity, which could also be modeled by theoretical calculations using appropriate programs. The field of fuel cell research is more open and has much more local contacts than lithium ion batteries, some co-workings are already set or on the way of setting.

## **Related publications**

Three project reports have been written this year within or connected to this project.

# PREPARATION, STRUCTURAL STUDIES AND OPTIMISATION OF BOROSILICATE GLASSES FOR HLW STORAGE APPLICATIONS

*Margit Fábíán*

## Objective

The final and safe storage of radioactive waste materials is nowadays an increasingly existing and problem to be solved urgently. The most feasible and accepted way for storage of high-level radioactive waste (HLW) is the vitrification process, where the active elements are melted and poured into glass form, and thereafter deposited in a deep geological formation, where the objective is to retain the radionuclides in the host rocks, and to block access to the biosphere. This report summarizes the activity of the first year of three years long OTKA project. As a first step I established a small radiochemistry laboratory for preparation of the planned glassy materials by rapid quench technique, which would open new possibilities for other projects as well.

## Methods

The structure of the glasses will be studied by different diffraction and spectroscopic techniques. For this work the building, which hosts the 10 MW Budapest research reactor (BRR), where I carry out my experimental work using the PSD neutron diffractometer, provides an ideal surrounding from the point of radioactive safety regulations.

I have purchased the high-temperature furnace (1700°C) from the LAC Company (Fig 1) and put it into operation on the second floor of the reactor building, and performed successful sample preparation pouring experiments using platinum crucible on the stainless steel plate.



Figure 1: Picture of the high-temperature electrical furnace.

## Results

Based on the experience of our previous studies, I had synthesized three new glassy samples: the so-called Matrix of composition  $55\text{SiO}_2 \cdot 10\text{B}_2\text{O}_3 \cdot 25\text{Na}_2\text{O} \cdot 5\text{BaO} \cdot 5\text{ZrO}_2$  (mol%), 90w%Matrix+10w% $\text{Ce}_2\text{O}_3$  and 90w%Matrix+10w% $\text{Nd}_2\text{O}_3$ . Ce stays for the hazardous radioactive Pu, while Nd for Uranium. Samples prepared from oxides:  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  ( $^{11}\text{B}$  isotope) are strong network formers;  $\text{Na}_2\text{O}$  is a network modifier; while  $\text{BaO}$  and  $\text{ZrO}_2$  serve both as network modifier, glass and hydrolytic stabilizers. The glasses were melted under atmospheric conditions, at temperatures between 1350 and 1450°C in platinum crucibles. Neutron diffraction (ND) measurement were performed at the BRR using the PSD diffractometer ( $\lambda_0 = 1.068 \text{ \AA}$ ). ND measurements indicate that the new compositions are stable glassy samples, no crystalline phase was detected. The Ce and Nd are structurally well integrated. Fig. 2 displays the ND experimental spectra, which show that our samples are fully amorphous.

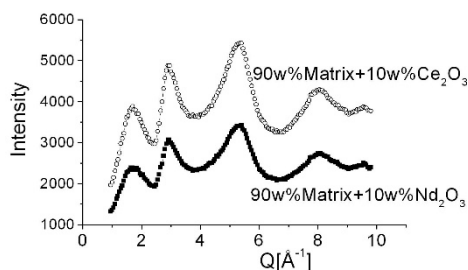


Figure 2: Neutron experimental spectra for Matrix glass+ $\text{Ce}_2\text{O}_3$  (circle) and Matrix glass+ $\text{Nd}_2\text{O}_3$  (square).  
Composition of the Matrix glass:  $55\text{SiO}_2 \cdot 10\text{B}_2\text{O}_3 \cdot 25\text{Na}_2\text{O} \cdot 5\text{BaO} \cdot 5\text{ZrO}_2$

The evaluation of the chemical-physical glass properties and the nuclear element capacity with the composition of the borosilicate glasses will be analyzed with the results of the structural characterization.

## Remaining work

We have a small laboratory which is suitable for vitrification of radionuclides with preparation of wide range of glassy samples. The next steps will be the structure study of the prepared new samples, and preparation of new formulation of borosilicate-based glass samples and optimization of glassy samples containing radioactive elements.

# RATE COEFFICIENTS OF HYDROXYL RADICAL REACTIONS WITH PESTICIDE MOLECULES AND RELATED COMPOUNDS: A REVIEW

*Erzsébet Takács, László Wojnárovits*

## Objective

The aim of this work was to prepare a rather thorough literature survey of the rate coefficients ( $k_{OH}$ ) published on  $\cdot OH$  reactions with pesticides and related compounds. For some of the molecules (actually for the most frequently used ones) several published  $k_{OH}$ 's are available, for example 2,4-D, MCPA, fenuron, diuron, linuron, atrazine, simazine, molinate. Sometimes there are considerable differences between the published values: the lowest and highest value may differ by one order of magnitude. We intend to help those, who may use these  $k_{OH}$ 's, e.g. for modelling degradation mechanisms or for investigating the fate of pollutants in the environment.

## Methods

The rate coefficient data were collected, evaluated and selected from papers and databases. By analysing the methods of  $k_{OH}$  determination and the  $k_{OH}$ 's obtained we select the most probable values by disclosing the unrealistic ones and making averaging for the seemingly reliable rate coefficients.

## Results

Rate coefficients published in the literature on hydroxyl radical reactions with pesticides and related compounds are discussed together with the experimental methods and the basic reaction mechanisms. Recommendations are made for the most probable values. Most of the molecules whose rate coefficients are discussed have aromatic ring: their rate coefficients are in the range of  $2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ – $1 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . The rate coefficients show some variation with the electron withdrawing–donating nature of the substituent on the ring. The rate coefficients for triazine pesticides (simazine, atrazine, prometon) are all around  $2.5 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . The values do not show variation with the substituent on the s-triazine ring. The rate coefficients for the non-aromatic molecules which have C=C double bonds or several C-H bonds may also be above  $1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . However, the values for molecules without C=C double bonds or several C-H bonds are in the  $1 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ – $1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  range.

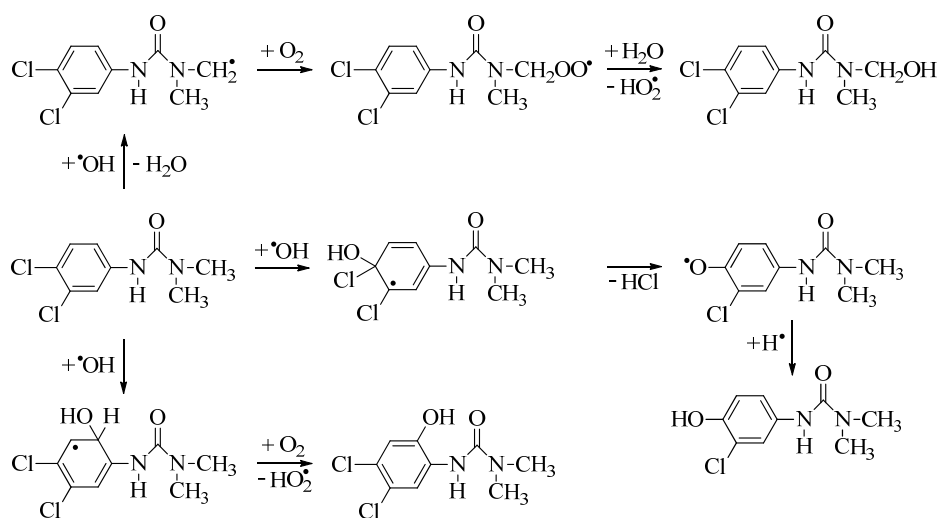


Figure 1: Suggested mechanism for OH radical reaction with urea compounds

## Remaining work

We plan to continue this work studying the degradation of antibiotics as target molecules.

## Related publications

- [1] L. Wojnárovits, E. Takács: *Rate coefficients of hydroxyl radical reactions with pesticide molecules and related compounds: a review*, Radiation Physics and Chemistry **96**, 120-134 (2014)
- [2] T. Csay, R. Homlok, E. Illés, E. Takács, L. Wojnárovits: *The chemical background of Advanced Oxidation Processes*, Israel Journal of Chemistry **54**, 233-241 (2014)

# DEVELOPMENT OF HIGHLY ENERGY-EFFICIENT DATA CENTRE INFRASTRUCTURE

*Endre Börösök, Csaba Farkas, Bálint Hartmann, Szabina Török, Veronika Oláhné Groma*

## Objective

The design of a complex power supply infrastructure and the satisfaction of the concentrated high energy demand is a constant challenge for data centre owners. Furthermore, economics of the operation and ideas of sustainability are getting more and more attention lately as well. A new concept was created; green data centres are designed to minimize the effect on the natural environment. One of the primary goals of such units is to decrease the energy needs both for the computing infrastructure and the supporting systems (e.g. thermal management), which can be achieved by increasing the efficiency of processes and/or by integrating renewable energy sources.

The research is based on an ongoing development cooperation between MTA EK and Persecutor Ltd., supported by the Hungarian Government's "PIAC\_13" programme. The project aims to develop a new, highly energy-efficient data centre infrastructure, which is able to supply IT needs at a high level, while minimizing power losses and exploiting the potential of locally available renewable energy sources. The two focus areas are: the use of energy storage in data centres and decreasing power losses in the distribution and power conversion infrastructure. After extensive review of the literature, evaluation criteria are defined in both topics to allow the future owner of the data centre to properly compare different technology and topology options.

## Methods

The project is well-aligned to the international trends, aiming to develop green data centre infrastructures. The difference is that in this case energy efficiency related to the information and communication technology (ICT) is not part of the investigations, but infrastructure issues are put into focus. The first phase of the project defined the boundary conditions of the research by evaluating possible energy sources and infrastructure location taking into consideration both strengths and weaknesses. The general energy model of a data centre was also defined, and a map of future locations was generated. These are utilised later, when evaluating the use of different energy sources based on their nature and local availability.

The second and third phase of the project laid more emphasis on technical questions of the research; technological processes, operational models, installed devices and materials are selected. Possible use of energy storage was examined from several aspects, like efficiency, lifetime and maturity. Tools to decrease power in the distribution infrastructure were selected.

## Results

Results considering energy storage have shown that means of both heat and electricity storage could be successfully applied in a data centre environment to decrease peak needs and to significantly decrease operation costs of the infrastructure. Results considering power losses have clearly proven that the majority of losses is generated by low loading of the elements of the technological chain, especially the UPS.

## Remaining work

The final phase focuses on the implementation of the results of previous phases. Detailed proposals are elaborated for selected geographical locations, determining maximal and optimal size of the data centre infrastructure.

## Related publication

B. Hartmann, Cs. Farkas, K. Sánta: *Development of an Energy Efficient Data Center Infrastructure – Use of Energy Storage and Decrease of Power Losses*, IEEE PowerTech Eindhoven 2015 – submitted

# ANALYSIS OF CLEARANCE PROCEDURES IN HUNGARY AND OTHER EU-COUNTRIES

*Tamás Pázmándi, Péter Zagyvai*

## **Objective**

The Hungarian Atomic Energy Authority (HAEA) and the Centre for Energy Research of the Hungarian Academy of Sciences (MTA EK) with „Frédéric Joliot-Curie” National Research Institute for Radiobiology and Radiohygiene (NRIRR) as assignees negotiated a research contract for studying the clearance of materials with radioactive content from regulatory control. The principal goal of the project was elaboration of recommendations (in the form of a guidance publication) for the improvement and standardization of authority activities concerning clearance in virtue of international directives and „best practices” of certain European countries.

The term „clearance” (sometimes termed as „release”) refers exclusively to facilities, devices, objects and materials previously under radiological control where activities subject to occupational and public health physics regulations were practiced. Clearance should be based on radioanalysis of material samples and objects in the course of which the most possible number of radioactive components are qualified and quantified; then concentrations found are compared to standardized clearance levels (CL) which in turn are related to a committed effective dose of 10  $\mu\text{Sv/a}$  taken as negligible (warranting no further protective actions) deduced from the dose/risk dependence characterizing the stochastic effect of ionizing radiations.

## **Methods**

In recent years general safety standards (Council Directive 2013/59/Euratom, IAEA General Safety Requirements Part 3 (2014)) were published setting a clear distinction between exemption and clearance procedures and publishing extensive data tables on the appropriate general CLs. However, “background” materials describing the deduction of general (unconditional) and particular (casual, conditional) CLs are necessary to be studied for the reliable interpretation of them and especially for defining new CLs for “unusual” (e.g. spallation product) radioisotopes and new types of application. Some compilations of previous research activities (e.g. EU Radiation Protection #122/I (2000)) published detailed description of selected scenarios comprising items for release, dispersion and exposure. After appropriate parameterization these “parallel” scenarios result in specific effective doses in  $[(\mu\text{Sv/a})/(\text{Bq/g})]$  units; the maximum of which then translates to CL. Practices of European countries (among them that of Germany, Sweden and Bulgaria were studied) are rather different in applying these predefined levels and/or prescribing the deduction of new, more characteristic ones.

## **Results**

According to the scheduled new Hungarian regulatory system, clearance should result in cleared traditional (non-radioactive) waste, reused or recycled material, devices, buildings and sites. Authority permit should be obtained by the licensee upon submitting a detailed safety analysis in a process applying for a general (unconditional) or specific (casual) clearance. Specific clearance (sometimes also termed as conditional) means that physical and chemical form of starting and/or cleared materials or objects are strictly defined. This is not a requirement in general clearance. CLs are available in international compilations containing widely accepted and justified data but – especially in case of specific clearance – it is also possible for the applicants to present exposure scenarios and thus individual CLs of their own for the authorities.

## **Related publication**

T. Pázmándi, P. Zagyvai: Research report EK-SVL-2014-263-01-01-00 - OAH-ABA-38/14-M (2014) (in Hungarian)



## **VII. RESEACH REACTOR UTILISATION**

# UPDATE OF THE BAGIRA-1 IRRADIATION RIG

*Ildikó Szenthe, Gábor Uri, Attila Kovács, Ferenc Gillemot*

## Objective

Neutron irradiation is one of the most severe ageing processes for structural and functional materials used in fission and fusion reactors. Since many research reactors have been shut down in Europe, the demand for new irradiation facilities is increasing. To study the radiation ageing phenomena, the "BAGIRA 1" irradiation rig operated since 1998 in the Budapest Research Reactor. Altogether 32 different irradiations were performed using this facility, among them reactor steels for fission reactor material study, stainless steel samples for fission and fusion reactors, tungsten, titanium for the ITER setup have been irradiated and tested. Two other irradiation rigs (BAGIRA 2 and BAGIRA 3) were also developed and operated. Until now a lot of operational experience was collected, and the irradiation requirements also changed calling for an update of the BAGIRA 1 rig. The objective of this work is to reduce the irradiation temperature scatter, the quantity of the radioactive waste and to simplify the preparation of the target holders, the target upload and withdraw. The upgraded rig will also be capable to irradiate functional and other materials (dielectric ceramics, heat and electrical insulation materials, fuel claddings) beside the metallic components.

## Methods

The design of the BAGIRA1 rig was updated. The new design partially used the spares of the BAGIRA 1 rig to reduce the production time and costs. The updated rig is named "BAGIRA4" and uses the new control system of the BAGIRA3 rig. The irradiation device consists of two main structural elements. The outside pipe reaches into the core from the upper part of the reactor, and is cooled by the reactor cooling water. Inside the target and in the target holder is a nitrogen - helium mix atmosphere. A new target upload and withdraw system was developed to reduce the radioactive waste of the target holders and simplify the target transportation into the hot cells using the target transportation pipe of the reactor. This pipe limits the target size, consequently the target was divided into 6 small size packets, each of them can be withdrawn separately. The size of the new target packet is 22\*25\*60 mm and within this volume material samples of different size and shape can be irradiated. The temperature regulation is made by the change of the ratio of the helium and nitrogen inside the rig. The change of the gas mix controls the heat removal from the gamma heated targets. The temperature of the packets are measured and registered separately. An auxiliary electric resistance heating is used to adjust the temperature of each packet separately within a  $\pm 5^{\circ}\text{C}$  range. The combination of electric resistance and gamma heating allows the irradiation of samples with different temperatures within the same reactor run. The target packets can be withdrawn separately, allowing the operators to reach different irradiation fluences and study the so called "Flux effect". Two design variations are elaborated: for low temperatures (up to max  $350^{\circ}\text{C}$ ) the target holder and the structural parts of the inner structure at the reactor core level are made from aluminium, for higher irradiation temperatures these parts can be made from titanium alloy. The outside pipe is water cooled and the temperature of its structural material is practically equal to that of the cooling water, consequently it can be used for both high and low temperature irradiation. A safety valve and a breaking disc ensures that the gas pressure inside the rig can't exceed the safety limit.

Each packet can include one or more dosimetry foil sets to measure the irradiation dose.

## Results

The task for 2014 was to elaborate the upgraded rig design. The main drawings of the BAGIRA 4 rig are ready, all design and material selection problems have been solved, moreover, the low temperature version is under production in the workshop. The missing materials are being purchased.

## Remaining work

The rig is planned to be built during the first quarter of 2015 and the test operation will be performed during the first half of the year. There are already several contracted irradiation tasks for the BAGIRA 4.

# OPTIMIZATION OF PGAA AND COMPLEMENTARY TECHNIQUES FOR METAL ANALYSIS

*Boglárka Maróti, László Szentmiklósi, Tamás Belgya*

## Objective

Improvement of the elemental composition determination by PGAA in contemporary and archaeological metals. Besides the major and minor chemical components, structural information can be obtained using complementary methods.

## Methods

XRF technique is a widespread non-destructive method in archaeological metal research, even though its reliability is limited by the small penetration depth of the X-rays. In contrast, PGAA is a bulk analytical method, and provides information about the whole irradiation volume. PGAA technique alone has limitations in metal analysis due to inherent nuclear properties (e.g. neutron absorption cross sections, distribution of strong gamma-rays and their background continuum) of many metallic elements. Evaluation of the complex gamma spectra is time consuming, and in most cases only the major and the minor components could be determined. Imaging of neutron attenuation by the samples was utilized using the NORMA station too.

## Results

A new measurement setup was installed at the NIPS-NORMA station, by replacing the standard 23% efficiency HPGe detector with a low energy germanium (LEGe) detector. Better energy resolution (Figure 1a) and symmetrical peak shapes improved the selectivity and made the peak fitting procedure much easier and faster. In this case, the LEGe detector was placed into the BGO Compton-suppressor, therefore the background level could be significantly decreased compared to the bare LEGe setup used in the pilot experiments in 2013.

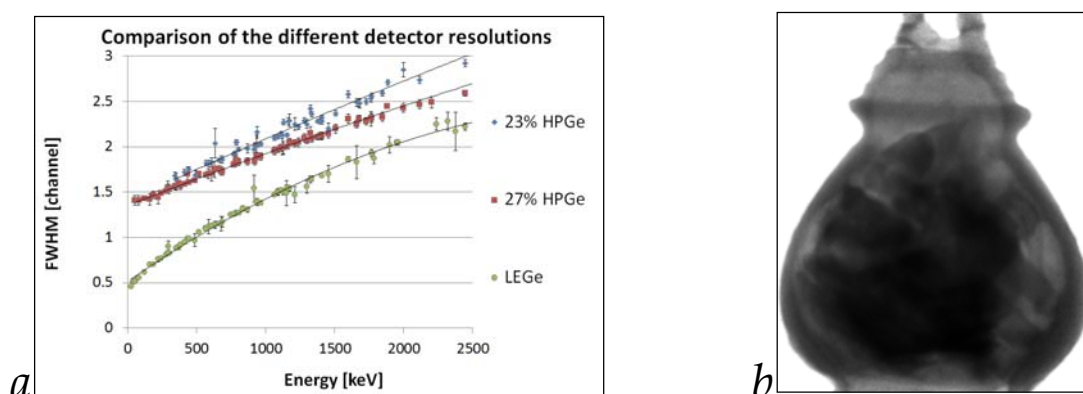


Figure 1: a, Resolution (FWHM) of the detectors; b, neutron radiography image of the Ottoman bronze weight.

Systematic comparisons of the performances of methods were made for bronze standards using the XRF, the standard PGAA detector, the LEGe setup and the high-flux PGAA setup in Garching. The best results were obtained for Pre-Roman silver coins (silver-copper based alloys) using the LEGe setup. The results were compared to an experiment with the 23% detector setup. Smaller efficiency of LEGe enabled us to measure the whole coins due to its lower specific count rate, which resulted in better representativity. It was also concluded that a higher selectivity was achieved. An article based on these results was submitted to a journal in December 2014 [1]. Ag and Au-containing supported catalysts were also analysed with LEGe [2]. The Ag-Au interference was better resolved and the concentration uncertainty was significantly reduced. Bronze weights from the Hungarian National Museum were analysed with XRF, and an Ottoman weight was selected for a detailed study by PGAA and neutron radiography. The comparison of the two datasets revealed the heterogeneous structure of the object analysed.

## Remaining work

To apply these complementary techniques for the analysis of various alloys.

## Related publications

- [1] J. Corsi, B. Maróti, A. Re, Zs. Kasztovszky, L. Szentmiklósi, M. Torbágyi, A. Agostino, D. Angelici, and S. Allegretti: *Compositional analysis of a historical collection of Cisalpine Gaul's coins kept at the Hungarian National Museum*, Journal of Analytical Atomic Spectrometry (submitted)
- [2] Benkó T, Beck A, Frey K, Srankó DF, Geszti O, Sáfrán Gy, Maróti B, Schay Z, Applied Catalysis A **479** 103-111 (2014)

# RADIOGRAPHY AND TOMOGRAPHY AT CHANNEL NO. 2 OF BRR

*Zoltán Kis, László Horváth, László Szentmiklósi*

## Objective

To develop neutron imaging instrumentation and methodology at channel No. 2 of Budapest Research Reactor. The radiography station (RAD) at the thermal neutron beamline gives a possibility to study relatively large objects by thermal neutron-, gamma- and X-ray radiography, and to benefit from the complementary features of the different radiations.

## Methods

In the framework of an MTA infrastructure grant awarded to MTA EK, the RAD station has been receiving a significant upgrade (digital imaging and tomographic capabilities) in 2014. In addition to the old analog system, new imaging equipment was built around a state-of-the-art digital camera. The static radiography and tomography images are acquired by a new, large area sCMOS camera (Andor Neo 5.5 sCMOS 2560×2160 px, 16 bit pixel depth), whereas the dynamic radiography is accomplished by a low-light-level TV camera and a frame grabber card. The image detection is based on suitable converter screens.

The available screens (partly new ones) are as follows: for neutron radiography, scintillation screens with resolution of 50-200  $\mu\text{m}$ ; for gamma- and X-ray radiography, a NaI(Cs) single crystal with resolution of 200  $\mu\text{m}$ , or a ZnS screen with resolution of 100  $\mu\text{m}$ . To better fulfil demands from users there is a possibility to apply larger or smaller fields of view with lower and higher spatial resolution, respectively. Here altogether three different optical systems can be setup using the available lenses with 50 mm, 105 mm and 300 mm fixed focal lengths interchangeably coupled to the digital camera, as one can see in Fig. 1. The dynamic radiography will be done by a low-light-level TV camera (640×480 px) with a light sensitivity of  $10^{-4}$  lux. The imaging cycle of this camera is 40 msec, making possible real-time imaging. A zoom optics coupled to this camera gives a variable field of view. The two cameras can be used interchangeably in the light-tight camera box equipped with a rail system providing the necessary optical path length.

## Results

The basic parameters of the facility have been measured. It has two measurement positions along the neutron beam, which are used for dynamic (DNR) and for static (SNR) imaging with the measured L/D ratios of 170 and 195, respectively. The thermal neutron fluxes at the two sample positions are  $4.64 \times 10^7 \text{ cm}^{-2}\text{sec}^{-1}$  and  $3.38 \times 10^7 \text{ cm}^{-2}\text{sec}^{-1}$ , respectively. The beam has a neutron to gamma ratio of  $1.72 \times 10^5 \text{ cm}^{-2}\text{mR}^{-1}$  and a cadmium ratio of 3.3. The thermal to epithermal flux measured by the cadmium covered and bare gold monitor method is about 51. The beam diameter is adjustable up to a maximum of 230 mm at the SNR position. There is a possibility to use beam filters made of Cd and In layers, resulting in an energetically modified and somewhat lower flux of  $3 \times 10^6 \text{ cm}^{-2}\text{sec}^{-1}$ . The gamma-ray intensity in the neutron beam measured with thermoluminescence dosimetry by András Kovács (SBL) is about 8.5 Gy/h, making it possible to carry out gamma-radiography measurements. The ambient dose rate from neutrons at the position of the digital camera chip (20 mSv/h, measured by the reactor's dosimetry group) was found still too high to use the new digital camera continuously.

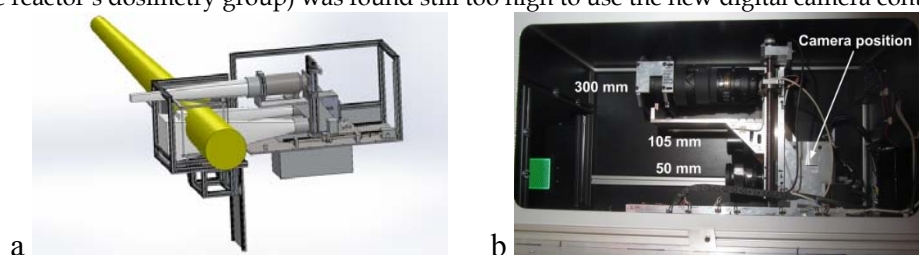


Figure 1: (a) The structural layout of the new RAD facility with the neutron beam and the three lenses used for static imaging. The system is to accomplish dynamic radiography using a low-light-level TV camera coupled to a zoom optics which is placed at the camera position. (b) The side view photo of the light-tight camera house showing the three lenses interchangeably coupled to the digital camera. Lenses with 50 mm, 105 mm and 300 mm fixed focal lengths are used for 3-step magnification to match the image to the chip size of the camera.

In parallel to the upgrade of the imaging system, the ANCARA supercritical loop was completed and the device is now ready for experiments.

## Remaining work

The adaptation of the NORMA-DAQ acquisition software, the detailed description of the imaging procedure and implementing computer-control of the large translation sample stage are still in progress. The improvement of the shielding of the digital camera system against neutrons is an ongoing task as well.

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# ASSEMBLY OF LOW-TEMPERATURE MEASURING STATION FOR MÖSSBAUER MEASUREMENTS

*Károly Lázár, Sándor Stichleutner*

## Objective

In the framework of the OTKA 81863 project the assembly of a low-temperature Mössbauer measuring station was accomplished. The apparatus can be used with liquid helium, providing means to perform eg.  $^{197}\text{Au}$  or  $^{193}\text{Ir}$  Mössbauer measurements. An appropriate position has also been constructed for the cryostat in one of the neutron beams supplied by the Budapest Neutron Centre, providing means to perform Mössbauer measurements with simultaneous “in-beam” generation and excitation of further sources.

## Method

The project principally aims to expand the applicability of Mössbauer spectroscopy.

## Results

The apparatus dedicated to low temperature Mössbauer measurements at 4.2 K with liquid He has been successfully assembled (Fig. 1). The basic part is a unique cryostat (CryoVac) designed particularly for in-beam measurements. It is appended with a WISSEL Mössbauer drive and data acquisition unit. Recycling of helium is provided by collection of the evaporated cooling medium into a 15 m<sup>3</sup> balloon, then the gas is compressed with a BRAUN compressor into a bundle of dozen high pressure cylinders, which can be returned for repeated liquefaction. To inaugurate the apparatus,  $^{197}\text{Au}$  spectra were recorded first. For illustration, one of these spectra is shown in Fig. 2. The measuring assembly in its final location adjusted to the neutron beam is shown in Fig. 3.



Figure 1:  
The low-temperature Mössbauer  
spectroscopy assembly

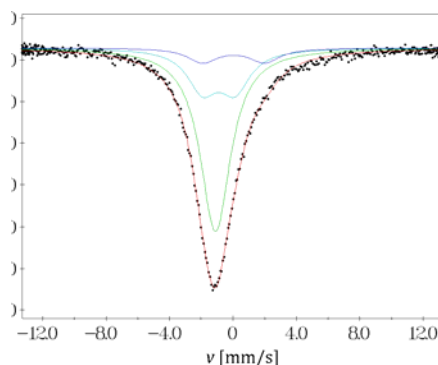


Figure 2:  
4.2 K Mössbauer spectrum of dithiolate  
stabilized 2 nm Au nanoparticles  
(note the decomposition of bulk and  
surface metal contributions)



Figure 3:  
The cryostat positioned in the neutron  
beam

## Remaining work

For the full completion of the in-beam measuring facility, the protection against the background radiation generated by the scattered neutrons is under construction.

## Acknowledgement

Financial support provided by the OTKA Grant No 81863 is gratefully acknowledged.

# PROVENANCE STUDY OF LITHIC RAW MATERIALS OF STONE TOOLS FOUND IN THE CARPATHIAN BASIN

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<sup>1</sup>Centre for Energy Research, <sup>2</sup>ELTE Department of Petrology and Geochemistry, <sup>3</sup>Hungarian National Museum, <sup>4</sup>Hungarian Institute of Geology and Geophysics

## Objective

Prompt Gamma Activation Analysis (PGAA) has been successfully applied to investigate various lithic assemblages, chipped and polished stone tools made of obsidian, flint, radiolarite, and greenschist-metabasite varieties (high-pressure metamorphite, nephrite, serpentinite, greenschist). The absolute non-destructive feature of PGAA is highly capitalised in the study of intact museum pieces. The present report is about the third year of an OTKA\* project, with a focused aim to map, analyse and characterise prehistoric resources, taking into consideration contemporary geographical and social endowments in the Central European region, as well as „long distance” raw material sources known to play important role in the European prehistoric exchange network. The expected results will contribute essentially to the knowledge on the system of contacts of the prehistoric communities by fingerprinting, characterising and tracing important lithic resources like obsidian, radiolarite, flint, high-pressure metamorphites, serpentinite and nephrite. The four-year project has started in April 2012.

## Methods

The research plan equally consists of geological sample collection on field work, conventional petrography (macroscopic and microscopic investigations), as well as instrumental analytical measurements. The leading analytical method applied is PGAA, mainly because of its absolutely non-destructive character. PGAA is applicable to quantify all the major components and some trace elements in lithic materials. It is unique in determination of the elements H and B. Occasionally, we plan to perform complementary measurements using XRF, INAA, EPMA or ICP-AES, ICP-MS. Other very important new method, the non-destructive SEM-EDX analyses was developed, partly in the framework of the current OTKA project. Besides PGAA, it has become a significant method to study the elemental and mineralogical composition of polished stone tools.

## Results

In the third year of the present project, we have continued the work with PGAA investigations of archaeological and geological samples made of obsidian, greenschist-metabasite varieties and various silex-type rocks from Hungary and – thanks to field works organized within the project, as well as to the CHARISMA Transnational Access – from Italy and Romania. Approximately 120 samples – both artefacts and raw materials – have been measured on PGAA and NIPS-NORMA stations of the Budapest Research Reactor. We have continued the measurements of valuable and unique greenstone archaeological objects (shaft-hole axes and hammers) by SEM-EDX method.

We have continued to investigate the obsidian and silex chipped stone tools of a very important Copper-Age culture of Erősd, which are represented in settlements of Eastern Transylvania and over the Carpathian mountains, Romania.

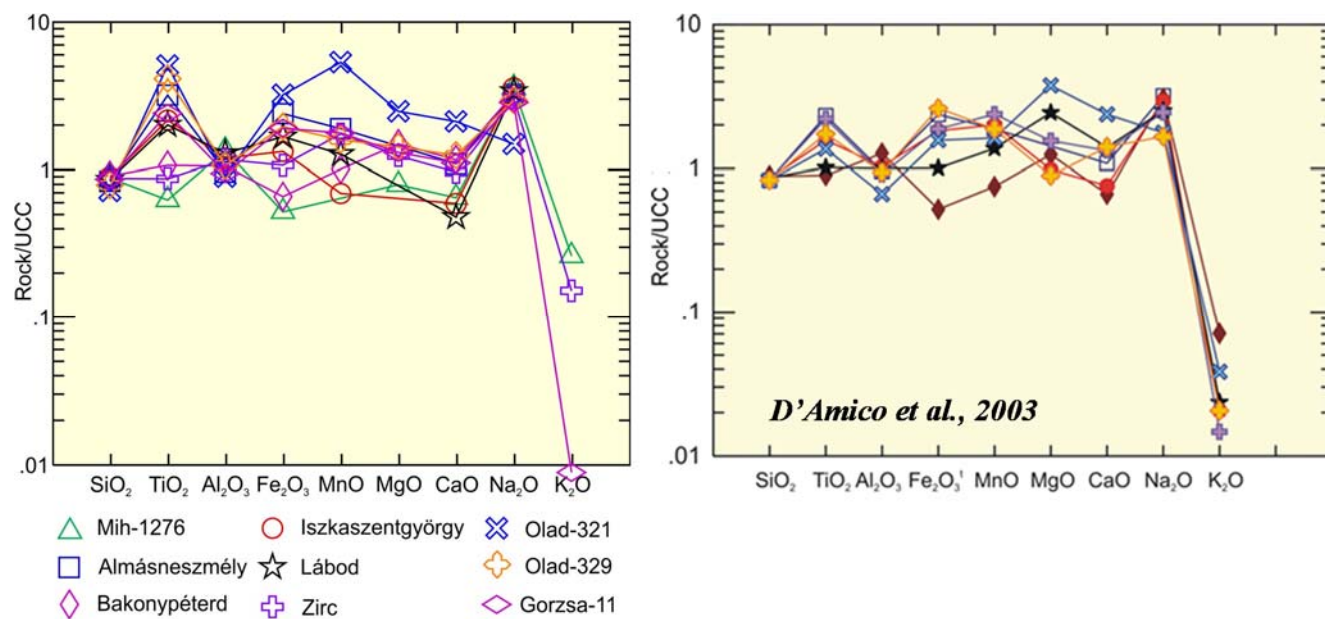
We have continued to construct a dedicated, internet accessible database of lithic objects and raw materials, which we intend to make accessible for scientists when a usable version is ready.

Because of unforeseen technical problems, less than expected PGAA measurements have been completed.

## Remaining work

In the final year, we will systematically continue the on-field collection of raw materials in the Central European region (Serbia, Romania, Bosnia, Czech Republic and Slovak Republic) and beyond, as well as non-destructive investigation of the prehistoric stone tools with preference on long distance trade items and building our comparative database.





**Figure:** Classification of stone HP-metamorphite stone tools based on PGAA (left) and on main rock types measured by XRF (right). Concentration values are logarithmic and normalised by Upper Continental Crust values (McLennan 2001). Mihálydy-1276: jadeitite, Almásneszmély: Fe-jadeitite, Bakony Péterd: jadeitite, Iszkaszentgyörgy: Fe-jadeitite, Lábod: Fe-jadeitite, Zirc: jadeitite, Olad-321: Fe-eclogite, Olad-329: Fe-mixed jades, Gorzsa-329: Fe-jadeitite.

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- [2.] B. Péterdi, Gy. Szakmány, Zs. Bendő, Zs. Kasztovszky: *Possible sources of nephrite artefacts found on Hungarian archaeological sites*, JADE2 meeting / Archeometriai Műhely, Budapest, 2014.03.21.
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- [4.] B. Péterdi, Gy. Szakmány, Zs. Bendő, Zs. Kasztovszky, K.T. Biró: *Magyarországi leletanyagokban fellelt „zöldkő” nyersanyagú csiszolt kőeszközök újabb archeometriai vizsgálati eredményei*, Kőkor Kerekasztal, 2014.12.05. ELTE Régészeti Intézet, Budapest
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- [6.] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Veluscek, C. Tuniz, Montagnari Kokelj: *Petrographic and geochemical comparison between the Copper Age "Ljubljana type" axes and similar lithotypes from Eisenkappler Diabaszug complex (southern Austria)* Journal of Archaeological Science 41 (2014) 511-522.
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- [8.] Gy. Szakmány, T. K. Biró, F. Kristály, Zs. Bendő, Zs. Kasztovszky, N. Zajzon: *Távolsági import csiszolt kőeszközök nagynyomású metamorfittokból Magyarországon / Long distance import of polished stone artefacts: HP metamorphites in Hungary*, Archeometriai Műhely 10/1 (2013) 83-92.
- [9.] Zs. Kasztovszky, K.T. Biró, Z. Kis: *Prompt Gamma Activation Analysis of the Nyírlugos obsidian core depot find*, Journal of Lithic Studies (2014) vol.1, nr. 1, p. 151-163.
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# BUDAPEST NEUTRON CENTRE - SCIENTIFIC UTILIZATION OF THE BUDAPEST RESEARCH REACTOR

*Rózsa Baranyai, Mihály Makai*

The Budapest Neutron Centre (BNC) coordinates the scientific utilization of the research reactor and makes available its facilities to the international neutron user community through the peer-review arrangement. BNC is a member of the European network of neutron centres and a partner in the EU Framework Programme projects (NMI3-II - Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy, CHARISMA - Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration and ERINDA - European Research Infrastructures for Nuclear Data Applications).

The CHARISMA project was completed in 2014. The final event of the four and half year project took place in Firenze, Italy. The aims of this conference were to present outcomes and activities of the project, highlight new research and innovative effective approaches for conservation and restoration of cultural heritage.

The NMI3-II is continuation of the NMI3 FP7 programme which integrates all major facilities in the field of neutron scattering and muon spectroscopy in Europe. This project opens opportunity to the more efficient use of the existing infrastructures.

BNC through its user programme offers 15 instruments to the international research community. Two of these instruments are located in the vertical channels of the reactor. The other 13 neutron instruments are installed directly to beam ports or to the neutron guides originated from cold neutron source. The cold neutron source provides very low energy neutrons with long wave lengths which allows to study structure and properties of the materials.

BNC receives around 50 beam time applications yearly. These proposals go through an evaluation procedure. Out of the accepted proposals BNC can provide beam time for those which get higher ranking than the average.

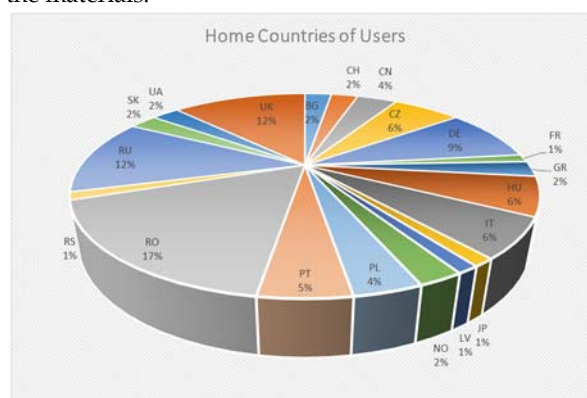
BNC is considered as a regional neutron centre, however, the last year statistics show that it became really international. Users from 20 countries got access to its facilities.

We continued the tradition and organized the 6<sup>th</sup> User Meeting, which usually is a half-day programme with user presentations and some short talks about the developments at BNC instrumentations.

BNC is helped by its International Scientific Advisory Council (ISAC), constituted of 15 renowned experts from various research establishments in Europe. At its last annual meeting the advisory board discussed the strategic issues of the extension of the Budapest Research Reactor (BRR) operation and BNC participation in the Central European Research Infrastructure Consortium (CERIC). CERIC provides integrated services for users in the field of chemistry, medicine, optics, micro- and nano-technologies, high-tech materials, environment, energy and cultural heritage.

University education as well as postgraduate and professional training in the nuclear field is an important task of BNC. BNC organizes the Central European School on Neutron Scattering every year. This school gives an introduction to the neutron techniques with a special emphasis on the hands-on-training at BRR's facilities. The school also provides a forum for presentation and discussion of actual research work of young scientists.

BRR is one the founder members of the first research reactor coalition, called Eastern European Research Reactor Initiative (EERRI). EERRI has a big potential of hosting nine reactors from seven countries. The wide variety of the research reactors and their utilization programmes allow for EERRI to offer any type of experimental works usually performed at research reactors: from beam experiments through various types of neutron activation analysis, fuel investigation, material science, radioisotope production to education and training. The coalition works most effectively in the field of education and training. In 2014, EERRI, with the support of the International Atomic Energy Agency, organized two training programmes: 8<sup>th</sup> and 9<sup>th</sup> EERRI Group Fellowship Training Course on Research Reactors.



# EXTENSION OF THE CERTA VITA SYSTEM BY THE MONITORING OF BUDAPEST RESEARCH REACTOR

*Csaba Horváth, Gábor Házi*

## Objective

The CERTA (Centre for Emergency Response, Training and Analysis) VITA system, developed by MTA EK, maintains an online data link with the four units of Paks NPP and the Hungarian Atomic Energy Authority (HAEA). It collects and displays more than 500 selected data from each unit and from the full-scope simulator of the NPP. In 2013 further development of this system was started with the aim to extend the capabilities of CERTA VITA with online monitoring of safety related measurement data of Budapest Research Reactor (BRR).

## Methods

Relevant measurements of BRR had been selected and a few groups were formed from these data based on the role of the measurements they play from safety point of view. Relations and conditions between data in a group are used to determine the status of the so-called critical safety functions (CSF), such as: subcriticality, core cooling, heat removal, primary circuit integrity, inventory. By definition: safety functions are a group of automatic (or manual) actions that prevent core melt or minimize radiation releases to the public. In general, CSFs are in relation with safety barriers, since as long as a CSF class is maintained, the corresponding barrier remains intact. Therefore, by evaluation of CSFs, we can determine the status of the safety barriers. In each measurement cycle the critical safety functions are evaluated, the corresponding status of the safety barrier is determined and monitored by the CERTA VITA system. Different colors are used to characterize the status of each CSF: green – normal operation, yellow - potential danger, etc.

## Results

In 2014 the system development has been finished and now, after a verification and validation period, the system is in full operation.

Fig. 1 shows a screenshot taken from the critical safety function monitor during the testing period.

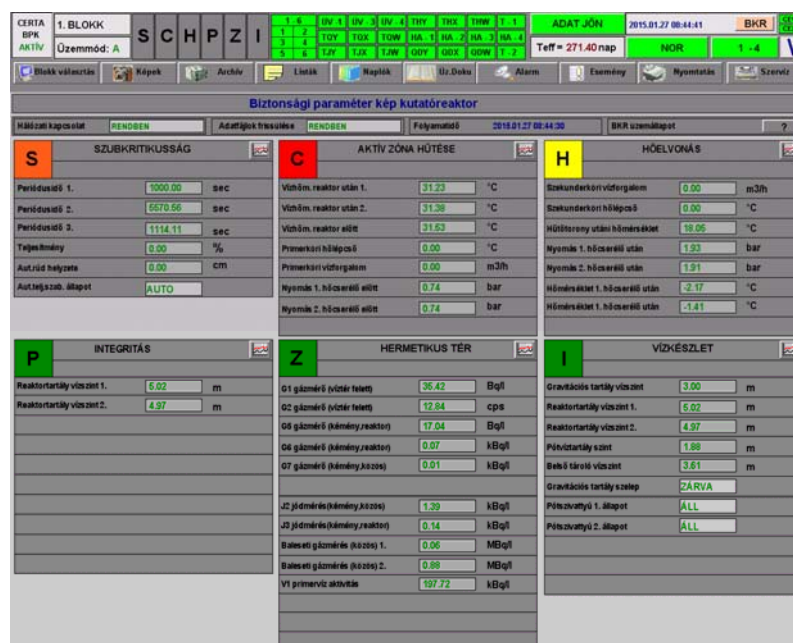


Figure 1: Critical Safety Function Monitor of BRR in the CERTA VITA system

## Remaining work

Although no work remained concerning the BRR, the development of CERTA VITA system will not be finished. Recently, HAEA requested an offer from MTA EK for an extension of CERTA VITA system. The objective of this extension is to online monitor the signals of the severe accident measurement system developed recently in Paks NPP. To establish this development a concept study will be prepared in 2015.

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# COMBINATION OF NEUTRON COINCIDENCE COUNTING AND NEUTRON IMAGING FOR DETECTING LOW AMOUNTS OF $^{235}\text{U}$

*László Szentmiklósi, Zoltán Hlavathy, Zsuzsanna Kovács*

## Objective

The fissile content of unknown materials can be measured by active neutron coincidence counting. This method is based on the detection of neutrons originating from neutron induced fissions. In order to improve the detection limit of the method by several orders of magnitude, the cold neutron beam of the Budapest Neutron Centre was used for irradiating the samples.

Between 2010 and 2011, we have established the method for combining cold neutron irradiation with neutron coincidence counting, elaborated the technical details and showed that it is a highly sensitive non-destructive method to determine the  $^{235}\text{U}$  content of unknown materials. We have proven that for a given geometry the detected rate of double coincidences is linear to the  $^{235}\text{U}$  content, and that it is independent of the chemical environment of the samples to the first approximation.

However, the statistical analysis of the results has shown that the scattering of the data was larger than statistically reasonable. We ascribed this to the inaccuracy of the sample positioning and to the different shape of the samples. In the years 2011-2012, we designed and realised the world's first Prompt Gamma Activation Imaging - Neutron Tomography facility called NORMA (Neutron Optics and Radiography for Material Analysis), which is a combination of an analytical and an imaging tool. This combination circumvents the similar spatial uncertainties of the PGAA. In the present work, we combined neutron coincidence counting (NCC) with neutron imaging (see Figure 1) in order to make it more robust and reliable during its expansion to the analysis of real samples. After the calibration of the system, we investigated different uranium-containing materials, including U metal, fuel pellets and environmental samples.

## Methods

Neutron coincidence counting, neutron imaging, irradiation with cold neutrons.

## Results

Based on the neutron transmission images, the grayscale values are used to correct for the spatial inhomogeneity of the beam. The contour of the sample is overlaid to the beam spot and an average intensity was derived. This number was used to rescale the raw double event rates.

These renormalized double coincidences are shown in Figure 3. With the above procedure we achieved that the investigated liquid and power samples fit to a single calibration curve with excellent linearity. Moreover, data taken with the thermal and the cold neutron beam could also be analysed with success.

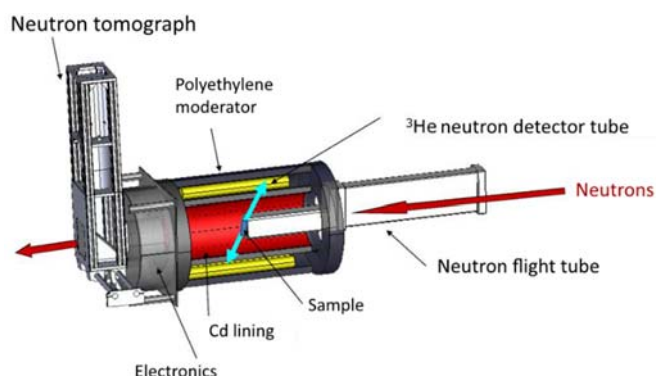


Figure 1: The neutron coincidence setup with the imaging camera

In environmental samples we were able to detect the signals of 10-20 ppm U from a 1-2 g sample. On the other hand, massive uranium pellets up to 2.5 g U-content were measured to check the other end of the dynamic range. In conclusion we demonstrated that this method is suitable for the determination of the  $^{235}\text{U}$  content in the  $\mu\text{g}$  and  $\text{mg}$  range and above, throughout many orders of magnitude.

## Remaining work

We will continue to provide support for the engineering of the facility and we will contribute to the implementation of the facility in 2013 on site. We will host another 2 guests for training in nuclear analytical techniques.

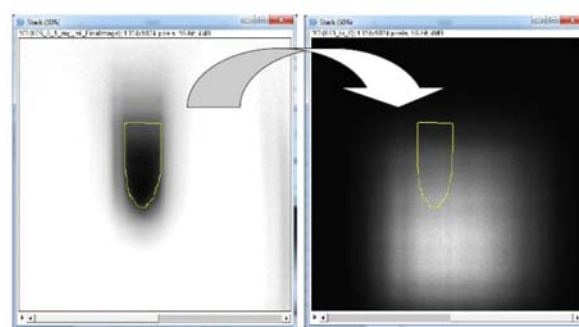


Figure 2: The sample holder is overlaid on the beam spot

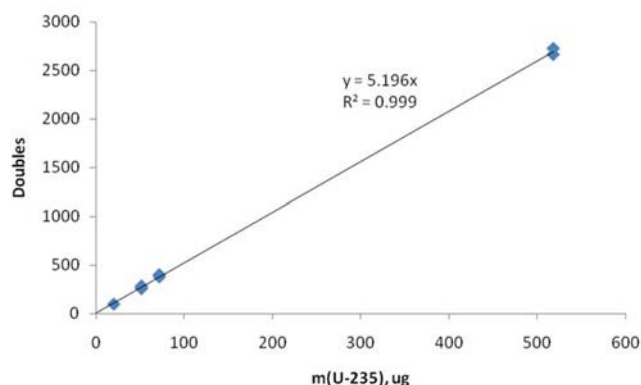


Figure 3: The corrected doubles vs. mass of  $^{235}\text{U}$

# CHARISMA - CULTURAL HERITAGE ADVANCED RESEARCH INFRASTRUCTURES: SYNERGY FOR A MULTIDISCIPLINARY APPROACH TO CONSERVATION/RESTORATION

*Zsolt Kasztovszky, Boglárka Maróti, László Szentmiklósi, Zoltán Kis, László Rosta\*, György Káli\*, Zoltán Szőkefalvi-Nagy\*, Imre Kovács\**

*\*Wigner Research Centre for Physics, Hungarian Academy of Sciences*

## Objective

CHARISMA is an EU-funded integrating activity project carried out in the FP7 Capacities Specific Programme "Research Infrastructures". The project – which lasted from October 2009 until March 2014 – provides transnational access to most advanced scientific instrumentations and knowledge allowing scientists, conservators-restorers and curators to enhance their research at the field forefront. Transnational Access programmes offer European scientists to carry out their experiments utilizing 3 different and complementary groups of facilities (ARCHLAB, MOLAB and FIXLAB) through a service embedded in a multidisciplinary environment involving material science and artwork conservation / restoration. The Budapest Neutron Centre – with the leadership of Wigner Research Centre for Physics and in cooperation with the Centre for Energy Research – offers non-destructive investigations of objects with Cultural Heritage significance (i.e. archaeological finds and other art objects), as a Transnational Access provider.

## Methods

The following facilities are available for CHARISMA users within the BNC consortium:

- Prompt Gamma Activation Analysis (PGAA) and Neutron Induced Prompt Gamma Spectrometer (supplemented with PGAI/NT unit): applicable for determination of bulk elemental composition with the optional tomography and elemental mapping of large objects – at the Centre for Energy Research
- Time of Flight Neutron Diffraction, Triple Axis Spectrometer and Small Angle Neutron Scattering: applicable for non-invasive micro structural and phase analyses at the Wigner RCP
- External milli-beam PIXE and compact XRF: applicable to determine the near-surface elemental composition – at the Wigner RCP.

## Results

In 2014, the last 4 projects, proposed by European scientists, have been completed and a continuation of a previous project has been done. Limestone archaeological objects (idols) have been measured. The pieces originate from a Calcolithic settlement of Perdigoes, Portugal, 4th-3rd millennium B.C. Compositions of archaeological objects have been compared with those of local or regional raw materials in order to determine the provenance of the objects. Secondly, so-called "nomad" (6. c. AD Sarmatian) bronze mirrors have been investigated, in order to identify manufacturing technologies or workshops within the Carpathian basin. It was aimed to identify specific compositions characteristic for Pannonian and Barbarian finds. Partly connected to an OTKA project, obsidian and silex chipped stone tools of a very important Copper-Age culture of Erősd have been studied. The aim was to classify the major rock types that have been used for tools production and, as far as possible, to determine their provenance. In a continuation of a previous project, composition of Celtic and Medieval silver drachms from Northern Italy have been measured with PGAA and XRF, in order to identify different coinage and also to reveal the course of inflation during the 4<sup>th</sup> to 1<sup>st</sup> century B.C. Finally, we have continued to investigate the effect of Cl on the corrosion process of archaeological (Roman) iron nails. 3D distribution of Cl was studied using bulk PGAA, PGAI and neutron radiography.

With the help of compositional and structural results, users hope to gain information regarding the provenance or techniques applied to produce the objects, as well as information to support conservation actions needed. In most research projects, combinations of the available non-destructive methods, being complementary to one another, have been applied.

## Remaining work

The CHARISMA project is officially terminated. Evaluation of the experimental data and dissemination of the results, however, are still in progress. As a continuation of CHARISMA, we will carry on the research within the HORIZON 2020 project IPERION CH from 2015.

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## **VIII. MISCELLANEOUS**

# DIGITAL GEOMETRY

*Attila R. Imre*

## Objective

Statistical analysis of the size-distribution of fragments can give crucial information about the properties of the fragmented materials, as well as about the nature of the fragmentation process(es).

## Methods

Black-and-white SEM pictures were analyzed by the ImageJ program. For the statistical analysis, the modified Korcak-analysis has been applied.

## Results

To demonstrate the applicability of the modified Korcak-analysis, a well-known set of quasi-2D objects were used namely the continents and islands of the Earth. While the continents were formed mainly by fragmentation, the islands were formed by a secondary process, the relative upward/downward movement of the water level. As it can be seen in Figure 1, the exponents (slope of the linear fits) remarkably differs for the continents (formed by primary fragmentation) and for the islands (formed by the secondary upward-downward movement). With this result, it can be shown that the modified Korcak-analysis is applicable to separate primary and secondary processes.

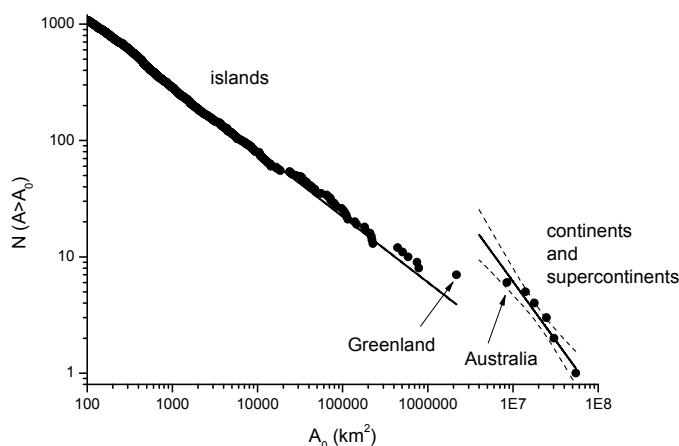


Figure 1: Size-distribution of the islands and continents

An interesting “byproduct” of this work is, that now one can define “islands” and “continents” by their intrinsic properties, instead of using an anthropogenic definition.

## Remaining work

Quantification of the effect of “accidental rotation” on the size distribution of fragmented pellets; with a proper quantification, the Korcak-analysis might be applied for the SEM-pictures of the fragmented pellets.

## Related publications

- [1] A. R. Imre: Description of the area-distribution of landmasses by Korcak exponent – the importance of the Arabic and Indian subcontinents in proper classification, Arabian Journal of Geosciences, in press, 10.1007/s12517-014-1481-0



# PHASE TRANSITIONS, METASTABILITY AND SUPERCRITICALITY

Attila R. Imre

## Objective

Metastability, supercriticality and sudden phase transitions were studied in various fluids with special emphasis on their applicability in energetics.

## Methods

Analytical methods and the ThermoC program were used to calculate stability limits and energy balance.

## Results

Metamaterials with negative compressibility constitute a promising group of novel materials with a wide variety of potential applications. Recently, a model was proposed for the construction of the structures with three-dimensional negative compressibility by utilizing successive destabilization of stable or metastable states and inducing phase transitions mimicking negative compressibility. In our study, it was demonstrated that similar concept is used by the nature and a nice example of this kind of metamaterial can be seen even in a glass of water [1].

For supercritical fluids one can find a wedge-shaped region called Widom region (starting at the critical point), where several physico-chemical quantities show anomalous behaviour. In our studies, several Widom lines of supercritical CO<sub>2</sub> have been computed with the Wagner–Span reference equation of state. The locations of the Widom lines in the pressure-temperature space are compared with the P–T range of the Snøhvit, Sleipner, Nagaoka and Ketzin reservoirs, which have been recently studied for their fitness for CO<sub>2</sub> sequestration, and two natural CO<sub>2</sub> storage analogues, Montmiral in France and Mihályi-Répcelak in Hungary. The consequences of leaking CO<sub>2</sub> crossing any of the Widom lines were discussed [2].

Adiabatic processes – very often used to approximate various processes in energetics – in the liquid – vapor two-phase region were studied with several equations of state. The comparison of the resulting isentropes, particularly their patterns in quality (fraction of vapour phase) vs. temperature diagrams, indicates that there are two different classes of fluids. One class shows a simple pattern where isentropes entering the two-phase region never leave it again; the other shows a more complicated pattern with reentrant isentropes, which may either cross the entire two-phase region or exhibit a retrograde behaviour; these classes are very similar to the “dry” and “wet” classes used in the description of various thermodynamic cycles of heat engines (for example the Organic Rankine Cycle). The existence of these two classes can be related to the shapes of entropy–volume or temperature–entropy curves, and these in turn to the temperature dependence of ideal-gas heat capacities. The two-phase isentrope that runs to the critical point approaches it with an infinite slope in the quality–temperature diagram. The slope is positive for reference equations of state, but negative for all other equations of state used in this work [3].

In the final part, condensation-induced water hammer (CIWH) were studied. During CIWH, a coldwater-surrounded hot steam pocket collapses. After the collapse, the water, rushing into the space formerly filled by steam acts as a hammer, hitting the pipe-wall. For the proper description of the process, the properties of the undercooled steam should be known. The traditional IAPWS (International Association for the Properties of Water and Steam) equation of state (used for steam tables) cannot be used to estimate the properties – relevant for CIWH-related calculations – of undercooled, metastable steam. An accepted test for the applicability of an equation of state in the metastable region is the comparison of the limit of undercooling calculated from the equation of state to the limit of undercooling estimated by an independent method. An independent method was developed by us, using the properties of liquid-vapour interfaces simulated by molecular dynamics; the limit estimated in this process was used to test various equations of state. Testing by several well-known equations of state, it has been found that the so-called volume-translated Peng–Robinson (vtPR) equation of state – which is able to describe stable phases too – can be used to describe the limit of undercooling. Although the accuracy of this equation for this property is much better than that of IAPWS, it should be still improved; therefore the development of an equation of state for metastable water is still a goal [4].

## Remaining work

Further studies of various fluids with special emphasis on the ones with applicability in energetics are still in progress.

## Related publications

- [1] A. R. Imre: *Metamaterials with negative compressibility – a novel concept with a long history*, Materials Science – Poland, 32(2014)126-129, DOI: 10.2478/s13536-013-0179-4
- [2] Attila R. Imre, Sergio E. Quinones-Cisneros, Ulrich K. Deiters: *Adiabatic processes in the liquid–vapor two-phase region - 1. Pure fluids*, Industrial&Engineering Chemistry Research, 53(2014) 13529-13542, dx.doi.org/10.1021/ie5022688
- [3] A. R. Imre, C. Ramboz, U.K. Deiters and T. Kraska: *Anomalous fluid properties of carbon dioxide in the supercritical region – Application to geological CO<sub>2</sub> storage and related hazards*, Environmental Earth Sciences, in press, DOI: 10.1007/s12665-014-3716-5
- [4] Attila Imre: *Energy release during the condensation of supersaturated steam; basic research related to water hammer phenomena*, Report – Hungarian Atomic Energy Authority, OAH/NBI-ABA-20/14-M, 2014 (in Hungarian)

# HIGH-ENERGY IONIZING RADIATION INDUCED DEGRADATION OF PERSISTENT ORGANIC CONTAMINANTS

*Erzsébet Illés, Erzsébet Takács, László Wojnárovits,  
Renáta Homlok, Gyuri Sági, Krisztina Kovács, Tamás Csay*

## Objective

The compounds studied are regularly detected in surface waters, because of their widespread application. A significant fraction is released to the environment by the wastewater treatment plants. The conventional water purification technologies are not effective enough in their degradation. The main aims of our work were to investigate the high-energy irradiation induced degradation of different persistent, harmful trace contaminants, like fenuron, monuron, diuron, amoxicillin, sulfanilamide (SAA) and 7 of its derivatives substituted on the N atom of  $-SO_2-NH_2$  in dilute aqueous solutions.

## Methods

For detection of intermediates generated by irradiation pulse, a radiolysis apparatus with kinetic spectrophotometric detection system was applied and for final products examination gamma radiolysis was used with analysis by UV-Vis and HPLC-MS-MS, ICP-MS techniques. The kinetics of chemical changes was followed by chemical oxygen demand (COD), total organic carbon content (TOC), total nitrogen content (TN) and toxicity measurements.

## Results

Because of the far-reaching and detailed research, in this report the decomposition of the contaminants will be presented with an example, an SAA derivative, the sulfamethazine (SMZ). The reactions of hydroxyl radicals (produced in water radiolysis) with SMZ were examined. As the pulse radiolysis experiments showed, the basic initial reaction was the hydroxyl radical addition to the benzene ring, forming cyclohexadienyl radical intermediates. In aerated solutions these radicals transformed to peroxy radicals. Among the first formed products aromatic molecules hydroxylated in the benzene rings or in some cases in the heterocyclic rings were observed by HPLC-MS/MS. COD measurements indicate that at the early reaction period of degradation one hydroxyl radical induces incorporation of 1.5 O atoms into the products. Comparison of the COD and TOC results shows gradual oxidation (Fig. 1). Simultaneously with hydroxylation, ring opening also takes place. The kinetics of formation of the inorganic ions,  $SO_4^{2-}$  and  $NH_4^+$  are similar to the kinetics of ring degradation, however, there is a delayed formation of  $NO_3^-$ . The latter ions may be produced in oxidative degradation of smaller N-containing fragments. The S atoms of sulfonamides after degradation remain in the solution according to ICP-MS measurements, whereas some part of the N-atoms leave the solution probably in the form of  $N_2$  based on TN measurements. The degradation goes through many simultaneous and consecutive reactions, and with the applied methods one can characterize the different stages of degradation.

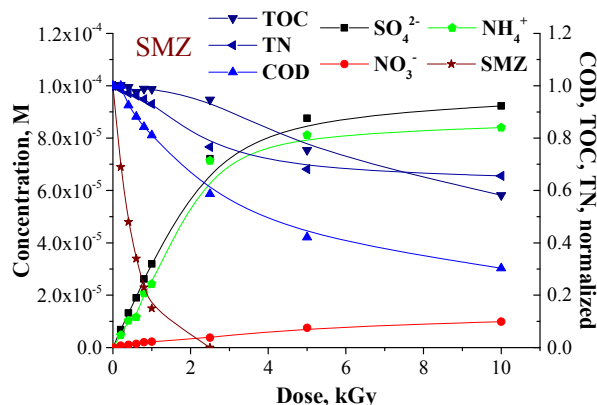


Figure 1: Comparison of the dose dependences of the degradation of SMZ, formation of  $SO_4^{2-}$ ,  $NH_4^+$  and  $NO_3^-$  (concentrations) and the normalized COD, TOC and TN values

## Remaining work

The research of fenuron, monuron, diuron, amoxicillin, sulfanilamide and its derivatives has been comprehensive, however some further investigations with them and experiments with other pharmaceuticals or other toxic compounds are still planned.

## Related publications

- [1] E. Illés, E. Szabó, E. Takács, L. Wojnárovits, A. Dombi, K. Gajda-Schranz: Ketoprofen removal by  $O_3$  and  $O_3/UV$  processes: kinetics, transformation products and ecotoxicity, *Science of the Total Environment* **472**, 178-184 (2014)
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- [6] K. Kovács, V. Mile, T. Csay, E. Takács, L. Wojnárovits: *Hydroxyl radical-induced degradation of fenuron in pulse and gamma radiolysis: kinetics and product analysis*, Environmental Science and Pollution Research **21**, 12693-12700 (2014)
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- [9] Gy. Sági, T. Csay, L. Szabó, E. Takács, L. Wojnárovits: *Szulfonamid antibiotikumok OH-gyök indukált lebontásának analitikai megközelítése híg vizes oldatokban*, Őszi Radiokémiai Napok 2014, Balatonszárszó, Magyarország, 2014.10.13-2013.10.15. Budapest: MTA Radiokémiai Bizottság, pp. 49-52. (ISBN: 978-963-9970-50-2) (2014)
- [10] L. Szabó, T. Tóth, G. Rácz, E. Takács, L. Wojnárovits: *Amoxicillin átalakulásai in vitro oxidatív környezetben*, Őszi Radiokémiai Napok 2014, Balatonszárszó, Magyarország, 2014.10.13-2013.10.15. Budapest: MTA Radiokémiai Bizottság, pp. 53-57. (ISBN: 978-963-9970-50-2) (2014)
- [11] E. Illés: *Radiolysis and other advanced oxidation processes for degradation of non-steroidal anti-inflammatory drugs in dilute aqueous solutions*, PhD thesis (date of defence 02.07.2014) (2014)

# SYNTHESIS OF CELLULOSE DERIVATIVE BASED SUPERABSORBENT HYDROGELS BY RADIATION INDUCED CROSSLINKING

*Erzsébet Takács, László Wojnárovits,*

*Tamás Fekete*

## Objective

Hydrogels are three dimensional networks capable to absorb high amount of water. They have numerous practical applications like, diapers, controlled release drug delivery systems. Hydrogels were prepared by ionizing radiation induced crosslinking in aqueous solutions of four cellulose derivatives (carboxymethylcellulose sodium salt – CMC-Na, methylcellulose – MC, hydroxyethylcellulose – HEC and hydroxypropylcellulose – HPC). In a complex approach, the effects of synthesis parameters on the gel properties including mechanism of water diffusion were investigated and compared under the same conditions.

## Methods

5 to 40 w/w% solutions were prepared in deionized water.  $^{60}\text{Co}$   $\gamma$ -source was used for irradiations. The gel fraction (GF) was calculated by the equation:  $\text{GF}(\%) = (W_1/W_0) \cdot 100$ ,  $w_0$  and  $w_1$  are the sample weight before and after extraction, respectively. The degree of swelling  $Q = W_s - W_d/W_d$ ,  $W_s$  and  $W_d$  are the masses of the swollen and dry samples. Swelling kinetics were described using two models: Second-order kinetics:  $dQ_t/dt = k(Q_{eq} - Q_t)^2$ , Power-law:  $Q_t/Q_{eq} = kt^n$ , where  $t$  is time,  $Q_t$  and  $Q_{eq}$  are the degree of swelling at time  $t$  and equilibrium,  $k$  and  $n$  are constants.

## Results

Based on systematic investigations with four cellulose derivative hydrogels prepared by  $\gamma$ -irradiation (CMC-Na, MC, HEC and HPC) it has been proven that the hydrophilic-hydrophobic character of the substituent is the determining factor in swelling properties. In pure water, second-order swelling kinetics described well the swelling behavior of all gels. The diffusion mechanism of the solvent into the polymer network was shown to be anomalous.

In pure water the hydrophilic CMC-based hydrogel shows the highest swelling ability, while less hydrophilic derivatives (HPC and MC) can absorb much less water. However, the high water uptake is accompanied by high electrolyte sensitivity. In solutions, modeling the real environment of potential hydrogel applications, HEC shows the best absorbing capacity. The key question of cellulose based hydrogel applications in real environment seems to be a proper hydrophilic/hydrophobic balance.

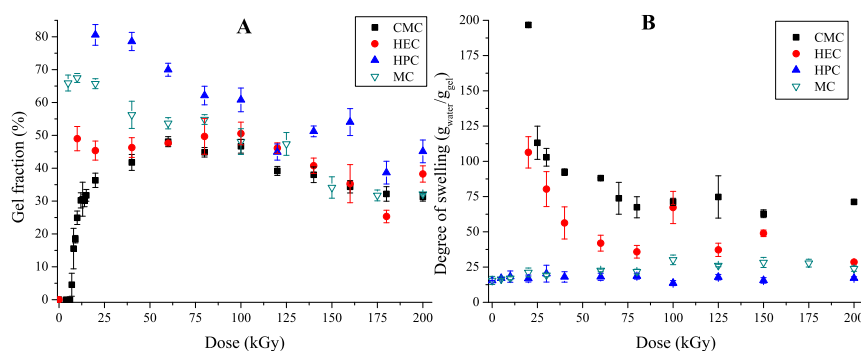


Figure 1: Effect of dose on gel fraction (deionized water, 48 h) (a) and degree of swelling (deionized water, 24 h) (b) of various cellulose-based gels (20% solution)

## Remaining work

As a continuation of the work we intend to decrease the dose necessary for the synthesis of mechanically stable hydrogels with acceptable water uptake capacity by adding monomers to the solutions of the cellulose derivatives before irradiation. The results will be summarized in a PhD thesis.

## Related publications

- [1] T. Fekete, J. Borsa, E. Takács and L. Wojnárovits: *Synthesis of cellulose derivative based superabsorbent hydrogels by radiation induced crosslinking*, Cellulose, **21**, 4157-4165 (2014)
- [2] T. Fekete, E. Takács, L. Wojnárovits and J. Borsa: *Radiation-induced synthesis of hydrogels from water soluble cellulose derivatives in the presence of crosslinking agent*. IRaP 2014, Ionizing Radiation and Polymers in Jeju island, Korea, October 5-9 2014. Invited talk (E. Takács)
- [3] T. Fekete, E. Takács, L. Wojnárovits and J. Borsa: *Radiation-induced synthesis of cellulose based superabsorbent hydrogels in the presence of monomer*, Autumn Radiochemistry Days 2014, Balatonszárszó, Hungary, 10.13.2014-10.15. 2014. Budapest: MTA Radiokémiai Bizottság, 2014. pp. 58-61. (ISBN: 978-963-9970-50-2)

# DEVELOPMENT OF NUCLEAR ANALYTICAL AND IMAGING TECHNIQUES, NUCLEAR DATA MEASUREMENTS, AND RELATED TRAINING ACTIVITIES

*László Szentmiklósi, Tamás Belgya, Zoltán Kis, Katalin Gmélíng, Boglárka Maróti*

## Objective

To develop our analytical and imaging capabilities and know-how in PGAA (Prompt-Gamma Activation Analysis), PGAI (Prompt Gamma Activation Imaging) / NT (Neutron Tomography) and low-level counting, to accurately determine related nuclear data, and to provide training and education for guest researchers and students

## Methods

( $n,\gamma$ ) measurements, evaluation of data and comparison to literature, computer programming, Monte Carlo modelling, teaching.

## Results

We performed highly accurate ( $n,\gamma$ ) measurements on elemental targets, such as Na, and on enriched isotopes of W, Eu and Gd. The evaluation of such data is completed in close collaboration with the colleagues at the Berkeley National Lab. The measured intensities were extended with DICEBOX calculations to make the de-excitation scheme more complete. The results were published in several papers [1-6].

In collaboration with the colleagues at the Institute for Reference Materials and Measurements (IRMM) Geel, we investigated the prompt fission gamma rays from  $^{241}\text{Pu}(n_{\text{th}},f)$  reaction. This research has been initiated following the requests from the OECD/NEA [7-8].

Neutron irradiation at a cold and Maxwell-Boltzmann distributed beam and Accelerator Mass Spectrometry (AMS) have been innovatively combined, thus the cross-section ratio of  $^{235}\text{U}(n,\gamma)/^{238}\text{U}(n,\gamma)$  can be deduced this way directly from the atom ratio of the reaction products  $^{236}\text{U}/^{239}\text{U}$ , independent of any fluence normalisation. Our results confirm the values at the lower band of existing data and serve as important anchor points to resolve present discrepancies in nuclear data libraries.

As the last phase of the construction of the NORMA instrument, we designed, manufactured and installed a computer-controlled beam collimator made of  $^6\text{Li}$ -polymer in order to adjust the shape and size of the beam to the needs. The control software has been extended accordingly.

In the DÖME low level counting facility, as the continuation of the earlier studies, various coal slag materials were measured and published [11]. Absorbed dose rate and annual effective dose for inhabitants living in buildings made of these materials were evaluated, based on the calculations from the  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity concentrations.

The Monte Carlo simulation code for the calculation of the detector response function was implemented in geant4 9.6.p02 for the Ge13 and LeGe detectors. Efficiency and full spectrum calculations were made, and the results were compared to the experimental gamma spectra. A good agreement was found and the results were published [12]. A rigorous mathematical formalism has been derived to fit the efficiency curve of the HPGe detectors with special emphasis of the uncertainty budget calculation [13].

We successfully finished our bilateral T&T collaboration with Morocco in the field of prompt and conventional neutron activation analysis. We measured about 15 standard reference materials at both facilities and the results were systematically compared.

We participated in the domestic and international training of students and scientists:

- 7<sup>th</sup> Central European Training School on Neutron Scattering: Nuclear Analytical Techniques and Neutron Imaging: lectures and lab exercises
- We hosted undergraduate lab exercises for students from Budapest University of Technology and Economics, ELTE University (5 occasions, altogether about 60 students)
- A newly launched course at ELTE University for geologists: Advanced nuclear analysis methods and their applications in geochemistry research. Lecture slides and lab guides were prepared [14-15].
- Summer training (4 weeks) for a physicist M. Sc. student with portable XRF technique. A lab guide for pXRF was compiled [16].
- Summer training for Brazilian students (material science major, Univ. Miskolc)
- Participated in summer training for Saudi students, organized by the Surface Chemistry and Catalysis Dept.

## Remaining work

There above described international collaborations and development directions are prosperous, so further experiments and data analyses are foreseen.

## Related publications

- [1.] Basunia MS, Firestone RB, Révay Zs, Choi HD, Belgia T, Escher JE, Hurst AM, Kr̩t̩čka M, Szentm̩kl̩si L, Sleaford B, Summers NC *Determination of the  $^{151}\text{Eu}(n,\gamma)\text{Eu}$  and  $^{153}\text{Eu}(n,\gamma)^{154}\text{Eu}$  Reaction Cross Sections at Thermal Neutron Energy* NUCLEAR DATA SHEETS 119: pp. 88-90. (2014)
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- [3.] Choi HD, Firestone RB, Basunia MS, Hurst A, Sleaford B, Summers N, Escher JE, Révay Zs, Szentm̩kl̩si L, Belgia T, Kr̩t̩čka M *Radiative Capture Cross Sections of  $^{155,157}\text{Gd}$  for Thermal Neutrons*, NUCLEAR SCIENCE AND ENGINEERING 177:(2) pp. 219-232. (2014)
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- [7.] Oberstedt S, Billnert R, Belgia T, Brys̩ T, Geerts W, Guerrero C, Hambsch F-J, Kis Z, Moens A, Oberstedt A, Sibbens G, Szentm̩kl̩si L, Vanleeuw D, Vidali M *High-precision prompt- $\gamma$ -ray spectral data from the reaction  $\text{Pu}^{241}(n_{th}, f)$*  PHYSICAL REVIEW C NUCLEAR PHYSICS 90:(2) Paper 024618. 6 p. (2014)
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- [9.] Wallner A, Belgia T, Bichler M, Buczak K, Dillmann I, K̩ppeler F, Lederer C, Mengoni A, Quinto F, Steier P, Szentm̩kl̩si L *Novel Method to Study Neutron Capture of  $\text{U}^{235}$  and  $\text{U}^{238}$  Simultaneously at keV Energies* PHYSICAL REVIEW LETTERS 112:(19) Paper 192501. 6 p. (2014)
- [10.] Belgia T, Kis Z, Szentm̩kl̩si L *Neutron Flux Characterization of the Cold Beam PGAA-NIPS Facility at the Budapest Research Reactor* NUCLEAR DATA SHEETS 119: pp. 419-421. (2014)
- [11.] V̩lgyesi P, Kis Z, Szabó Z, Szabó C *Using the 186-keV peak for  $^{226}\text{Ra}$  activity concentration determination in Hungarian coal-slag samples by gamma-ray spectroscopy* J. Radioanal. Nucl. Chem. (2014) 302(1) 375-383
- [12.] Szentm̩kl̩si L, Belgia T, Maroti B, Kis Z *Characterization of HPGe gamma spectrometers by geant4 Monte Carlo simulations* JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY 300:(2) pp. 553-558. (2014)
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## Lecture slides and lab guides:

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- [16.] Be̩ta Rom̩sz, Bogl̩rka Mar̩ti, L̩szl̩ Szentm̩kl̩si: *A PRACTICAL GUIDE TO PORTABLE X-RAY FLUORESCENCE ANALYSIS OF ALLOYS AND MINERALS* p 1-22.

## M.Sc. Thesis based on our experiments:

- [17.] Andrew G. Lerch, *NUCLEAR STRUCTURE OF RHENIUM-186 REVEALED BY NEUTRON-CAPTURE GAMMA RAYS*, MSc thesis, Department of Engineering Physics Graduate School of Engineering and Management Air Force Institute of Technology (2014)

## **IX. INTERNATIONAL ACTIVITIES**



# APPLICATIONS OF PROMPT-GAMMA ACTIVATION ANALYSIS

Zsolt Kasztovszky, László Szentmiklósi, Boglárka Maróti, Katalin Gméling

## Objective

It was aimed to apply the prompt-gamma activation analysis to determine the samples' elemental composition. Research was performed in the fields of catalysis, material science, geochemistry and archaeometry. Within the project, the activities of the EU-funded NMI3-II and CHARISMA projects were supported, too.

## Methods

Principally, PGAA and NIPS facilities at a cold neutron guide of the Budapest Research Reactor were used to determine the elemental compositions of various samples. As complementary methods, NORMA imaging facility, in-situ catalytical characterization (e.g. titration), solid state nuclear track detectors (SSNTD), neutron activation analysis, X-ray fluorescence have been applied.

## Results

### Chemical catalysis

The catalyzed gas-phase oxidation of HBr ( $2 \text{ HBr} + 1/2 \text{ O}_2 \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ ) is a particularly attractive process to recover  $\text{Br}_2$  from HBr enabling the sustainable bromine-mediated upgrading of alkanes. We found that the HBr oxidation is catalyzed over Deacon catalysts under mild conditions. In situ PGAA has made a significant contribution in evaluating new generation of Deacon catalysts for HCl oxidation, now it was extended for the HBr oxidation, in collaboration with colleagues at ETH Zürich. We measured the HBr oxidation mostly over  $\text{TiO}_2$  under various conditions (feed composition and temperature) as well as conducted a few tests on  $\text{RuO}_2$ . We observed that  $\text{TiO}_2$  does not significantly change its bromine coverage upon increasing oxygen partial pressure, which could indicate a less strong effect of catalyst re-oxidation on the activity of this material. Further, it was found that  $\text{TiO}_2$  takes up more Cl than Br under comparable conditions and significantly less Br than Ru.

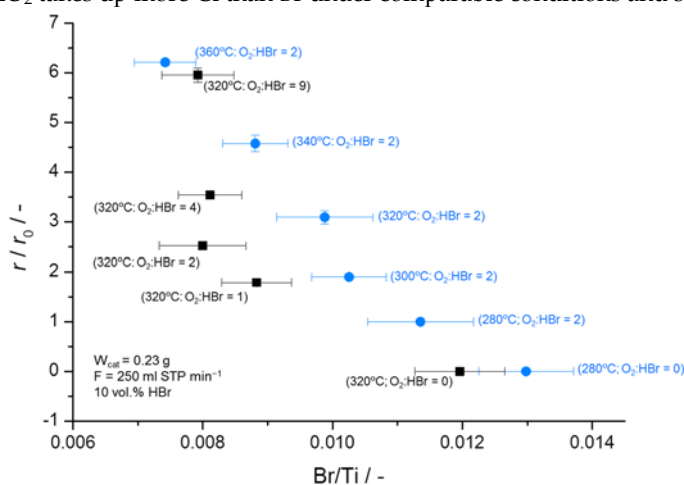


Figure 1: The Br uptake of  $\text{TiO}_2$  catalyst as a function of oxygen partial pressure (black symbols) and temperature (blue symbols)

### Material science

A pilot study to investigate sol-gel derived  $\text{SiO}_2$ -CaO bioactive glasses have been made on the PGAA station. The aim of the new 2015 experimental proposal that will be submitted by Pál Jóvári (MTA Wigner RCP) is to determine the compositional specifications of sol-gel derived glass compared to melt-quenched glass that result in their bioactivity.

As a continuation of our experiments since 2012, a second batch of Co-Re based alloys was prepared at the TU Braunschweig to supplement Ni-base Superalloys at ultra-high temperature ( $>1200^\circ\text{C}$ ) applications, such as turbines. We quantified the B content of Co-Re-Cr(-Ta) alloys by PGAA, whereas the spatial distribution of the boron in the alloys is being mapped with the SSNTD technique.

### Archaeometry

Partly related to a project supported by the Hungarian Scientific Research Fund (OTKA) and by CHARISMA EU FP7, compositions of stone axes made of nephrite, jadeite, metadolerite, blueschist, etc. have been determined in parallel with those of geological references. The aim of the study is to identify the origin of the raw materials (i.e. provenance of the objects). Based on PGAA measurements, we were able to differentiate between major rock types, in accordance with EDS-XRF measurements.

In another study, compositions of limestone archaeological objects (idols), found in the Calcolithic settlement of Perdigoes,

Portugal, 4<sup>th</sup>-3<sup>rd</sup> millennium B.C. have been measured. So far, no archaeometric approach has been done to these stone idols. Two main questions were aimed to answer: 1, Is it possible to differentiate raw materials used in the stone idols of the two types of funerary contexts? 2, Did these stone idols point to different provenances, with diversified raw materials (local / regional / unknown)? The compositions of the archaeological objects have been compared with those of local or regional raw materials. To evaluate homogeneity of the stone idols, the presence/absence of internal fractures, filled fissures, neutron radiography on NIPS-NORMA station was applied. For characterisation of near-surface compositional details, External Beam milli-PIXE of Wigner RCP was used.

We have continued to investigate the effect of Cl on the corrosion process of archaeological (Roman) iron nails. 3D distribution of Cl was studied using bulk PGAA, PGAI and neutron radiography.

Finally, compositions of so-called "nomad" (6. c. A.D. Sarmatian) bronze mirrors have been investigated, in order to identify manufacturing technologies or workshops within the Carpathian basin. It was aimed to identify specific compositions characteristic for Pannonian and Barbarian finds. It was also intended to find correlation between alloy composition, casting technique (studied by TOF-ND) and mirroring capacity.

### Geochemistry

We have continued analysis of volcanic rock samples from Antarctica (King George Island). The new geochemical results could be compared with those, which were last year measured from Deception Island. The geochemically analysed samples are also under geochronological (K/Ar) investigation at MTA ATOMKI.

Very unique meteorite microspherules from the Cheljabinsk region have been measured by PGAA and Scanning Electron Microscopy, and their Contrite-type classification was confirmed.

### Remaining work

Most of the spectra measured in 2014 are still under evaluation process. Successful collaborations are planned to continue.

### Related publications

- [1.] Mukherji D , Gilles R , Karge L , Strunz P , Beran P , Eckerlebe H , Stark A , Szentmiklosi L , Macsik Z , Schumacher G , Zizak I , Hofmann M , Hoelzel M , Rosler J *Neutron and synchrotron probes in the development of Co-Re-based alloys for next generation gas turbines with an emphasis on the influence of boron additives* Journal of Applied Crystallography 47: pp. 1417-1430. (2014)
- [2.] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Velušček, V. Szilágyi, C. Tuniz, E. Montagnari Kokelj, *Mineralogical And Chemical Constraints On The Provenance Of Copper Age Polished Stone Axes Of 'Ljubljana Type' From Caput Adriae*, Archaeometry, 56, 2 (2014) 175-202
- [3.] F. Bernardini, A. De Min, D. Lenaz, Z. Kasztovszky, P. Turk, A. Veluscek, C. Tuniz, E. Montagnari Kokelj: *Petrographic and geochemical comparison between the Copper Age "Ljubljana type" axes and similar lithotypes from Eisenkappeler Diabaszug complex (southern Austria)* Journal of Archaeological Science 41 (2014) 511-522.
- [4.] Kasztovszky Zs.: *Tűz és víz találkozása; obszidián a Kárpátokon innen és túl* (2014) Élet és Tudomány LXIX/2. 38-40.
- [5.] Kasztovszky, Zs., Biró, K. T., Kis, Z.: *Prompt Gamma Activation Analysis of the Nyírlugos obsidian core depot find*, Journal of Lithic Studies (2014) vol.1, nr. 1, p. 151-163.
- [6.] Mödlinger, M., Kasztovszky, Zs., Kis, Z., Maróti, B. Kovács, I. Szőkefalvi-Nagy, Z., Káli, Gy., Horváth, E., Sánta, Zs., El Morr, Z.: *Non-invasive PGAA, PIXE and ToF-ND analyses on Hungarian Bronze Age defensive armour*, J Radioanal Nucl Chem (2014) 300, 787-799
- [7.] Péterdi, B., Szakmány, Gy., Judik, K., Dobosi, G., Kasztovszky, Zs., Szilágyi, V., Maróti, B., Bendő, Zs., Gil, G., *Petrographic and geochemical investigation of a stone adze made of nephrite from the site Balatonőszöd*, Geological Quarterly 2014 58/1 181-192
- [8.] E. Abraham, M. Bessou, A. Ziégélé, M.-C. Hervé, L. Szentmiklósi, Zs. Kasztovszky, Z. Kis, M. Menu, Terahertz, *X-ray and neutron computed tomography of an Eighteenth Dynasty Egyptian sealed pottery*, Appl. Phys. A (2014) 963-972.
- [9.] D. Mukherji, R. Gilles, L. Karge, P. Strunz, P. Beran, H. Eckerlebe, A. Stark, L. Szentmiklosi, Z. Mácsik, G. Schumacher, I. Zizak, M. Hofmann, M. Hoelzel and J. Rösler, *Neutron and synchrotron probes in the development of Co-Re-based alloys for next generation gas turbines with an emphasis on the influence of boron additives*, J. Appl. Cryst. (2014). 47, 1417-1430.
- [10.] T. Benkó, A. Beck, K. Frey, D. F. Srankó, O. Geszti, Gy. Sáfrán, B. Maróti, Z. Schay, *Bimetallic Ag-Au/SiO<sub>2</sub> catalysts: Formation, structure and synergistic activity in glucose oxidation*, Applied Catalysis A: General 479 (2014) 103-111.
- [11.] K. Gmélíng, A. Simonits, I. Sziklai László, D. Párkányi, *Comparative PGAA and NAA results of geological samples and standards*, J Radioanal Nucl Chem (2014) 300:507-516

# APPLIED NUCLEAR METHOD: MÖSSBAUER SPECTROSCOPY

Károly Lázár, Sándor Stichleutner

## Objective

Various structural studies have been performed by applying Mössbauer spectroscopy.

## Method

Various types of Mössbauer spectroscopy have been used, namely with  $^{197}\text{Au}$  and  $^{57}\text{Fe}$  nuclei in transmission geometry and with  $^{119}\text{Sn}$  and  $^{57}\text{Fe}$  nuclei in conversion electron detection.

## Results

### $^{197}\text{Au}$

The apparatus dedicated to low temperature Mössbauer measurements at 4.2 K with liquid He has been successfully assembled and first  $^{197}\text{Au}$  spectra recorded. For illustration, some spectra are shown in Fig. 1.

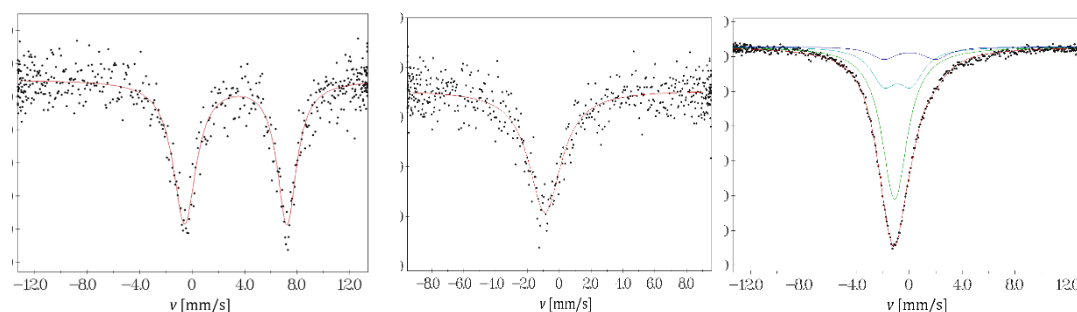


Figure 1:  $^{197}\text{Au}$  Mössbauer spectra recorded at 4.2 K. Left:  $[\text{Au}^{\text{I}}_2(9,9\text{-dimethyl-4,5-bis(diphenylphosphino)xanthene})_2]$  complex, for description see Deák et al., *CrystEngComm*, 16 (2014) 3192, center: 2 wt% bimetallic ( $\text{Au}_{0.8}\text{Ag}_{0.2}$ )/ $\text{TiO}_2$  catalyst, prepared in our Surface Chemistry and Catalysis Laboratory, right: dithiolate stabilized gold nanoparticles (diameter 2 – 3 nm), prepared at University of Szeged.

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Studies on structures of porous ferrisilicates have been continued. Particular attention has recently been paid to investigation of the bonding strength of iron to the porous framework. Probabilities of the Mössbauer effect for various species of iron in Fe-LTA, Fe-FER and Fe-MCM-41 structures have been compared in this respect [1].

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Double nuclei conversion electron Mössbauer spectroscopy studies have been performed on electrochemically deposited SnFe and SnNiFe alloys. Structures of alloys formed during direct current and pulse plating electrolysis are compared. The products of the direct current deposition are dominantly crystalline. In contrast, the pulse plating results mostly in formation of amorphous alloys [3].

## Related publications

- [1] K. Lázár: Variations in bonding of iron in porous ferrisilicates, *Hyperfine Interactions*, **226**, (2014) 99 – 109.
- [2] Deepshikha Singh, L. Kótai, K. Lazar, R.L. Prasad: EPR, Mössbauer and magnetic studies of coordination polymers of type  $[\text{Cu}_x\text{Fe}_y(\text{dedb}) \cdot 2\text{H}_2\text{O}]_n$  (dedb = dianion of 2,5 dichloro-3,6-bis (ethylamino)-1,4-benzoquinone) ( $x = 0\text{-}1$ ,  $y = 0\text{-}1$ ), *Solid State Sciences* (2014) doi:10.1016/j.solidstatesciences.2014.11.008
- [3] S. Stichleutner, G. B. Lak, E. Kuzmann, C.U. Chisholm, M. El-Sharif, Z. Homonnay, L. Sziráki, Mössbauer and XRD study of pulse plated Sn-Fe, Sn-Ni and Sn-Ni-Fe electrodeposited alloys, *Hyperfine Interactions*, **226** (2014) 15 – 25.

# PROGRESS AT THE NEUTRON ACTIVATION ANALYSIS LABORATORY

*Dénes Párkányi, László Szentmiklósi, Katalin Gméling, Ibolya Sziklai-László*

## Objective

Application of Neutron Activation Analysis (NAA) in environmental research, archaeology and geochemistry.

## Method

NAA, high resolution gamma-spectrometry with HPGe detector, Hypermet-PC and Hyperlab 2014 spectrum fitting software and  $k_0$ -based concentration calculation programs.

## Results

### *Instrument upgrade*

From a successful grant application it became possible to upgrade the aging infrastructure of the NAA laboratory. We purchased a state-of-the-art Ortec DSPEC 502 dual channel digital gamma spectrometer with zero dead time option. This device significantly outperforms the old signal processing chain in terms of energy resolution, peak shape, stability, count rate tolerance and dead time correction. A spectrum converter utility was prepared to feed the ORTEC spectrum format to Hypermet PC.

In parallel, an ORTEC HPGe detector with 55% efficiency (called as D5) was rebuilt into upright-standing configuration and put into regular operation, replacing the malfunctioning Ge(Li) counting system. As a result, two high-performance gamma spectrometers (D4 and D5) placed in low-level iron counting chambers are available for scientific work and another (D3) for routine activity measurements. All detectors were accurately recalibrated at up to 5 sample-to-detector distances.

For short-term irradiation of the samples, a pneumatic rabbit system is operational. Over the years its operation became unstable. The rabbit directing hardware, the front-end electronics have been partially replaced and the control software was upgraded with the help of the Reactor Dept. (József Janik, Csaba Katona). In order to extend the irradiation period, a new sample holder capsule with high melting point is being tested. The sample temperature determination inside the capsule, overall neutron flux characterizations and the investigation of the reproducibility/reliability of the irradiations were performed in the irradiation channel.

### *Software upgrade*

In 2014 we introduced the Hyperlab 2014.2 version for gamma spectrum analysis. For concentration calculation, we made an intercomparison between the so-far used RNAACNC, the Kayzero/Solcoi and the  $k_0$ -IAEA packages. We concluded that the best results could be obtained with the Kayzero, whereas in limited cases the  $k_0$ -IAEA package is also suitable.

### *Scientific utilization*

The results from an intercomparison between ICP-MS and NAA for the  $^{135}\text{Cs}$  determination have been published this year [1]. Comparison and combination of the PGAA and NAA technique have been further continued with additional geological reference materials and standards. NAA and PGAA proved to be good complementary analytical procedures to each other. Measurement results of the standards also show very good agreement with the recommended values [2]. A set of geological samples from the Antarctica (King George Island) have been analyzed. The chemical composition of those samples were already measured by other laboratories, thus inter-laboratory comparison is possible. Few samples from Deception Island (Antarctica) were also measured by NAA, which were previously measured with PGAA. The specialty had been the latest measurements is that the samples were not powdered, but chips of the whole samples were sealed into high-purity quartz ampules. Mineral separates from upper mantle xenoliths (olivine, ortho- and clino-pyroxene and spinel) were measured by NAA, and the results are comparable to in-beam NAA results performed at PGAA station in Garching in 2013. Most of the above mentioned measurements were performed by the end of 2014, thus their spectra are still under evaluation process.

### *Analytical Services*

The activity concentrations of characteristic fission and corrosion products in the BRR's primary cooling water and the chemical concentrations of different impurity components in various water systems of the BRR were measured to monitor the water quality. The activities of irradiated samples and flux monitors were also measured upon internal request.

## Remaining work

The data analysis of the completed experiments is in part still in progress. Further publications are foreseen.

## Related publications

- [1] Nagy P., Vajda N., Sziklai-L. I., Kovács-Széles É., Simonits A. *Determination of  $^{135}\text{Cs}$  in nuclear power plant wastes by ICP-MS and  $k_0$ -NAA*, J Radioanal Nucl Chem (2014) 300:615–627
- [2] Gméling K., Simonits A., Sziklai L. I., Párkányi D. *Comparative PGAA and NAA results of geological samples and standards*, J Radioanal Nucl Chem (2014) 300:507–51

# RESULTS OF THE HUNGARIAN-MOROCCAN BILATERAL INTER-GOVERNMENTAL COLLABORATION

László Szentmiklósi, Katalin Gméling, Zoltán Kis

## Objective

A Hungarian-Moroccan bilateral inter-governmental collaboration (TÉT-10-1-2011-0492) was established to promote the development of prompt gamma and conventional neutron activation technique (PGAA and NAA) at CNESTEN, Rabat, and their applications in environmental science and archaeology. The project started in March 2012 and lasted for 24 month.

## Methods

Application of the prompt gamma activation analysis methodology as described in the "Standard Operating Procedure of the Budapest PGAA-NIPS/NORMA-DÖME facility" (NAL-PGAA-01). Concentration measurement by  $k_0$ -NAA. Measurement of standard reference materials, quality control.

## Results

The SNL-SAND-II (PSR-0345/01) code was obtained from NEA data bank to estimate the energy distribution of a beam based on a set of irradiated activation monitors. In parallel, detailed calculations were completed with MCNP5 code to estimate the dose rates of the planned facility. It turned out that the direct radial beam of the TRIGA reactor contains too many fast and epithermal neutrons, and the gamma radiation from the reactor core is also rather high. As a result, sapphire and Bi filters were chosen to meet the health physics standards. In addition, the installation of a 3-4 meter neutron guide is proposed to get away from the direct view of sight.

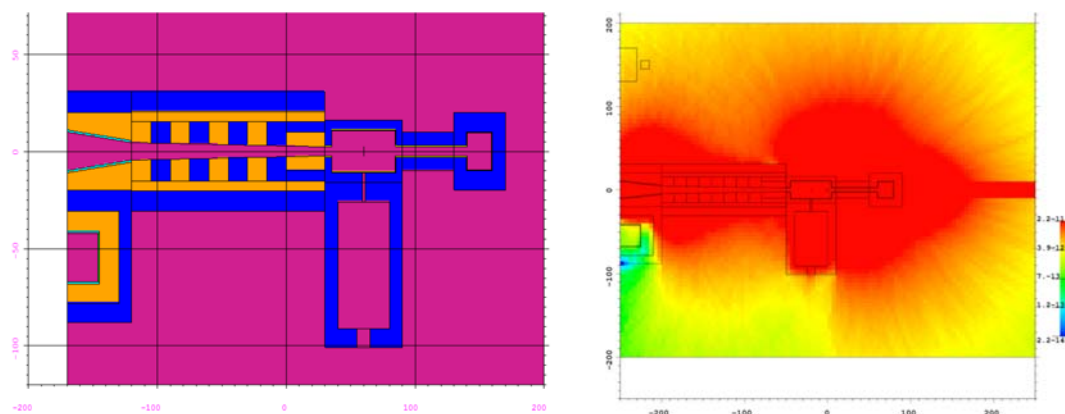


Figure 1: The scheme and MCNP5-calculated dose maps of the planned facility

With Hypermet-PC we calibrated the detectors at the NAA lab of CNESTEN at 5 distances from contact geometry to 250 mm. We determined the position of the Ge crystal within the detector housing by scanning with a Cs-137 source.

Finally, an intercomparison exercise was completed with about 15 geological and environmental standards, including the two NAA laboratories and the Budapest PGAA facility. The Budapest data were in good agreement with the certified values, therefore the analytical protocol was found to be appropriate. It was also concluded that the NAA and PGAA results well complement each other, i.e. the best-measurable elements of the two techniques are often complementary. The results were published in two papers [1-2].

## Remaining work

We will continue to provide support for the construction of the PGAA facility and expert advices in nuclear analytical techniques.

## Related publications

1. H. Bounouira, K. Embarch, H. Amsil, M. Bounakhla, M. Blaauw: *Neutron flux characterization of the Moroccan Triga Mark II research reactor and validation of the  $k_0$  standardization method of NAA using  $k_0$ -IAEA program*, J. Radioanal. Nucl. Chem., 2014, **300** (2) 465-471
2. K. Gméling, A. Simonits, I Sziklai L., D. Párkányi: *Comparative PGAA and NAA results of geological samples and standards*, J Radioanal Nucl Chem (2014) **300** (2) 507–516

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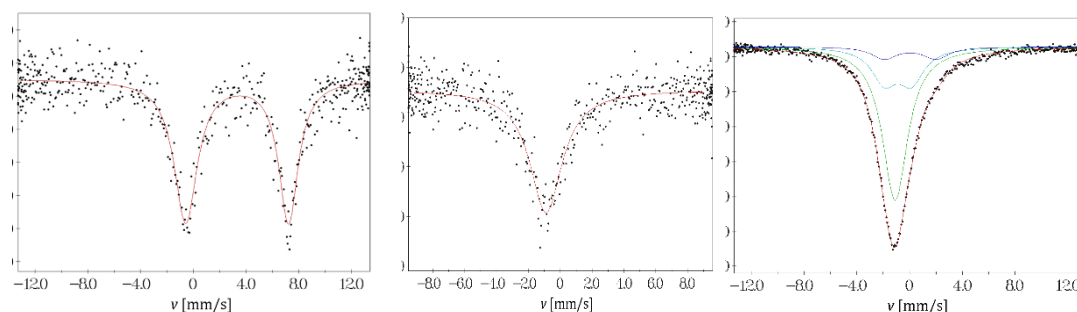


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# DEVELOPMENT, CHARACTERIZATION AND MODELLING OF SELF-POWERED NANOGENERATORS ON FLEXIBLE FIBROUS ASSEMBLIES

*Erzsébet Takács, Viktória Míle*

## Objective

The aim of the collaborative work is to develop and model the piezoelectric characteristics of fibrous assemblies consisting of zinc oxide (ZnO) nanowires prepared in the form of nonwoven structures. Out of nonwoven materials (viscose, polypropylene, Kevlar etc.) we chose viscose because of its higher hydrophilicity as compared to other materials. The aim of this work was the electrochemical deposition of large-scale single-crystalline ZnO nanotube arrays on the viscose substrate from an aqueous solution.

## Methods

The nanowires were grown on the surface of textile fibres (viscose) oriented in various alignments ranging from purely random to highly preferentially oriented structures. ZnO nanostructures were synthesized by two wet-chemical methods (hydrothermal and electrochemical) featuring low temperature (95°C) and atmospheric pressure onto nonwoven substrates. For the hydrothermal method applied,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and hexamethylenetetramine (HMTA) reagents were used. For the electrochemical method  $\text{ZnCl}_2$ , and KCl containing electrolyte with  $\text{H}_2\text{O}_2$  and/or  $\text{O}_2$  bubbling were applied. The surface morphology of the ZnO array films was studied by JEOL JSM-6700F scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV.

## Results

ZnO nanorods were formed by electrodeposition and by hydrothermal deposition on the surface of the textile fibre samples. We have found that the surface coverage was poor in the case of hydrothermal deposition of ZnO nanowire from precursor solution of 1-20 mM. Only a few random spots of the ZnO nanowires attached to the substrate appeared on the surface. Optimum precursor solution turned out to be 50 mM  $\text{Zn}(\text{NO}_3)_2$  and 50 mM HMTA equimolar precursor solution, and the optimum deposition time ranged between 25-30 hours. In this case ZnO nanowires were synthesized with appropriate surface coverage. The nanowires were mainly oriented vertically to the substrate surface.

The ZnO nanowires, deposited by hydrothermal method exhibit a perfect hexagonal faceted morphology (wurtzite structure crystals) with a diameter of 250 - 500 nm, and lengths of about 3-7  $\mu\text{m}$ .

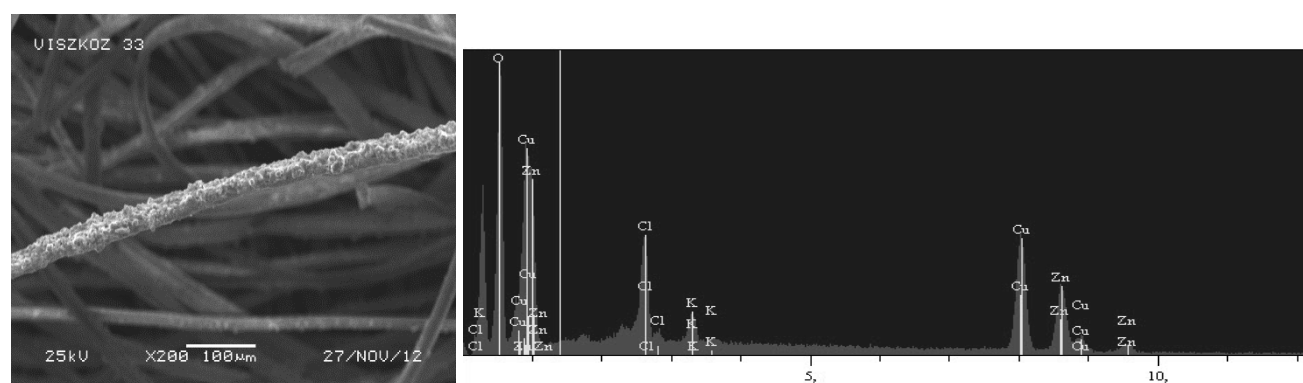


Fig. 1: SEM images and EDX analysis on copper coated viscose material after electrochemical deposition process from 5 mM  $\text{ZnCl}_2$  + 0.1 M KCl +  $\text{H}_2\text{O}_2$  with oxygen bubbling

## Remaining work

The project is finalized.

## Publication

M. Furkó, E. Fazakas, E. Takács: *Deposition of nanostructured ZnO with variable morphology by electrochemical and hydrothermal methods onto nonwoven materials*. Material Science Forum **812**, 41-46 (2015)



# URANIUM AGE DATING BY WELL-TYPE HPGe DETECTOR

A. Kocsonya, Zs. Kovács, C. T. Nguyen, L. Lakosi, I. Almási

## Objective

In the previous years a non-destructive method based on high resolution gamma-spectrometry was developed for age-dating of uranium samples. The method was tested and proved on several samples [1], [2]. These tests provided that the detection limit is <10 years for high-enriched uranium (HEU) samples depending on enrichment. In case of low-enriched uranium (LEU), the situation is not so good. With decreasing enrichment the limit of detection of age-dating is increasing. Therefore, the next challenge of the project is enhancing the sensitivity and precision of the method for LEU samples [2].

## Method

The method of uranium age-dating by gamma-spectroscopy is based on the measurement of the  $^{214}\text{Bi}/^{234}\text{U}$  activity ratio. In the course of steps of uranium purification and enrichment, daughter elements are removed from the sample. In time to follow these elements build up again. The elapsed time since the last chemical procedure can be calculated from the daughter-to-parent ratio. However, most of the daughters cannot be measured by gamma-spectrometry. The first nuclide, which can be effectively measured, is  $^{214}\text{Bi}$ .

Because of the low activity of the  $^{234}\text{U}$  daughters, the detection limit of uranium age-dating depends on the sensitivity of  $^{214}\text{Bi}$  detection. Since  $^{214}\text{Bi}$  comes from atmospheric radon ( $^{222}\text{Ra}$ ) as well, not only sensitive detection but also the reduction of radon background is essential.

The detection sensitivity can be increased by well-type detectors, which can provide rather efficient sample-detector geometry, due to the close  $4\pi$  solid angle. This year a new well-type HPGe detector was purchased, especially for uranium age-dating measurements. The new detector is a Canberra GCW6023 type, with 60% relative efficiency and 293 cm<sup>3</sup> active crystal volume. The purpose of the first measurement period was the testing of characteristics of the detector for uranium age-dating measurements and gaining experiences in this field.

## Results

Due to the high counting efficiency, in case of HEU samples the dead time of the system can be rather high even if the sample mass is only 1-2 grams. Since a significant number of counts comes from the low energy (<100 keV) region of the spectrum, the sample was covered by a 0.2 mm thick lead shielding to reduce the intensity, but the absorption at the relevant energy (609.3 keV) is negligible.

Another aspect of experimental circumstances is positioning the sample. The most evident position would be in the detector well. However, in this position the coincidence effect is rather significant. This means that in case of nuclides emitting more gamma-energies via cascade decay it has significant probability of counting more photons simultaneously, which gives a signal of summed energies (sum peak) of the incident photons. Even triple coincidences were recorded. The other factor limiting the sensitivity is the Compton-background from higher energy gamma-lines, mainly from  $^{238}\text{U}$  ( $\rightarrow$   $^{234\text{m}}\text{Pa}$ ), which decreases the detectability of the 609.3 keV line. Suggested by these limiting factors less compact measuring geometries were tested. Namely, the sample was positioned above the detector well, reducing hereby the probability of occurring sum peaks.

The age dating procedure was tested by samples enriched to 90%, 36%, and 4.6%, being available from the stocks of the institute. In case of HEU samples the results are consistent and they are in agreement with former gamma spectroscopy and mass spectroscopy results. In case of the 4.6% sample, the results proved that the method can be applied for this enrichment range. However, some uncertainties are not easy to consider. The correction for the coincidence effect is a rather complex procedure. Background subtraction is not so simple either, since the radon level changes from time to time. Measurement times can be rather long; even one week is possible. Therefore neither uncertainty nor detection limits may be sufficient.

## Remaining work

Due to the outlined complexity of the age dating of LEU samples, a little below half year work with the new device could provide only limited experiences and preliminary results. In the next period a more detailed account of several effects and factors will be necessary:

- Long term stability of the detector system
- Background subtraction and tracing radon level, decreasing radon level
- Optimizing measurement position, shielding, sample mass, if available
- Correcting detector calibration for the coincidence effect. Correction factors for measuring positions
- Expanding the range of LEU samples. Those of 2-5-10% enrichment are planned to test
- Age dating of the Nuclear Forensics ITWG Collaborative Materials Exercise 4 (CMX-4) samples (2014)

## Related publications

- [1] L. Lakosi et al.: *Development of Nuclear Forensics Methods and Techniques for Combating Illicit Trafficking of Nuclear and Other ...*, Application of Nuclear Forensics in Combating Illicit Trafficking..., IAEA TECDOC No. 1730 25 (2014)
- [2] C. T. Nguyen J. Zsigrai, L. Lakosi: *Uranium Age Dating by Gamma Spectrometry*, Proc. Int'l. Conf. Advances in Nuclear Forensics: Countering the Evolving Threat of Nucl. and Other Rad. ..., July 2014, Vienna, Austria, IAEA-CN-218/13

# DEVELOPMENT OF NATIONAL NUCLEAR FORENSICS LIBRARY

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## Objective

Illicit trafficking of nuclear and other radioactive material is a subject of serious concern due to the radiological hazard to the public and the environment as well as the security risks associated nuclear and other radioactive material out of regulatory control. The availability of tools to prevent and respond to incidents of nuclear smuggling resulted in the development of a new field known as nuclear forensics which can assist in law enforcements investigations and nuclear security assessments associated with a nuclear security event. Through nuclear forensic analysis, information on the history and on the potential origin of intercepted nuclear material can be obtained by investigating the characteristic parameters of such material. Analysis of data characteristics or signatures (e.g. isotopic composition of uranium, morphology features, age or production date, impurities, etc.) of this material provides insight to the industrial processes used in their manufacture. Despite the availability of these data characteristics, the experiences indicate that it is difficult to determine the origin and history of unknown samples without comparison data from known samples to facilitate the identification. To increase confidence in determining the origin and history of questioned materials, analysis of numerous comparison samples from the same and also different confiscations and batches with different origin is necessary. Another important element is the development by States of a National Nuclear Forensics Library to aid in national level comparisons of material out of regulatory control.

## Methods

In the frame of the project, investigation of the most important and informative/characteristic parameters (signatures) for nuclear forensics purposes was planned and to find for it novel methods and to characterize fully the seized materials originated from Hungarian confiscations within the next few years. As a first step in 2013 was a comprehensive review of relevant publications to include a search for promising new methods in other scientific disciplines. The following work in 2014 covered starting of extensive analysis and characterization of confiscated materials using different techniques, such as microscopy, gamma-spectrometry and mass spectrometry for creation of a relatively large and informative database.

## Results

In 2014 all the nuclear samples originated from Hungarian confiscations were analyzed by mass spectrometry for their conventional parameters (isotope ratios, enrichment, production date, morphology, surface, structure, physical parameters, impurities (rare-earth content and other elemental impurities), reprocessing). In the followings an example of the results is showed as a part of the future database and national nuclear forensic library. Following the results gained from the analysis the origin of the materials can be determined.

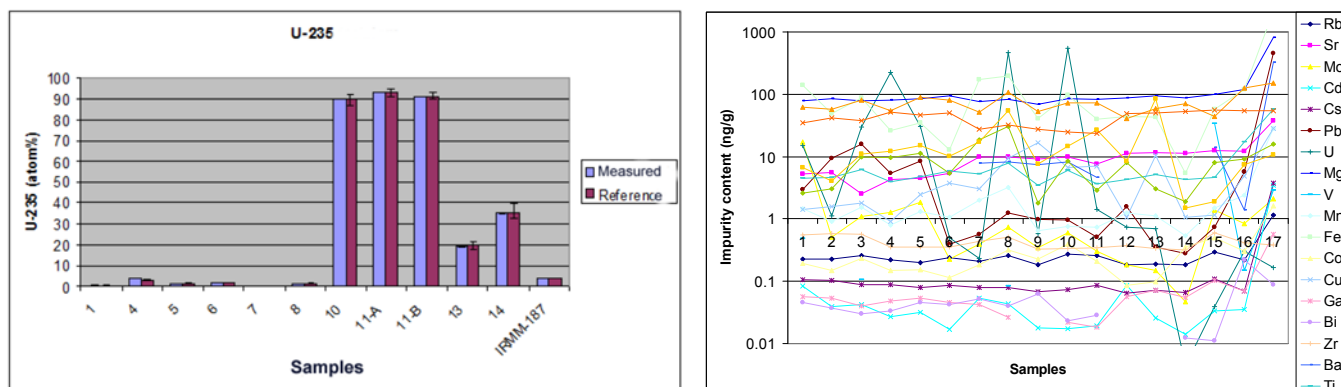


Figure 1: Signatures of confiscated materials: U-235 content (isotopic composition), left and impurity profiles, right

## Remaining work

Full characterization of the confiscated materials using further different techniques as Scanning Electron Microscopy or X-ray diffraction technique needs more years. Therefore, this project is an ongoing work together with IAEA in a Coordinated Research project which is running until 2015. The analysis of the seized nuclear materials is continued using also new parameters and developments. Finally, a full database will be created and compiled relevant to the development of a national nuclear forensics library.

## Related publications

- [1] É. Kovács-Széles, I. Almási: *Nemzeti törvényszéki analitikai könyvtár (Library) készítése a lefoglalt nukleáris anyagok részletes elemzésével*, OAH MMT research report, OAH-NBI-ABA-15/14-M (2014)
- [2] É. Kovács-Széles: *Progress Report on Coordinated Research Project (IAEA CRP: J02003) with the title of: „Identification of High Confidence Nuclear Forensics Signatures for the Development of National Nuclear Forensics Libraries”, 2014*

## ABBREVIATIONS

AER	Atomic Energy Research
ANCARA	MTA EK-BME NTI Budapest supercritical water test facility
AOO	Anticipated Operational Occurrence
AOT	Advanced Oxidation Technologies
ASA	acetylsalicylic acid
ASTM	American Society for Testing and Materials
ATWS	Anticipated Transient Without Scram
BEXUS –	Balloon Experiment for University Students
BME NTI	Budapest University of Technology and Economics, Institute of Nuclear Techniques
BNC	Budapest Neutron Center
BRR	Budapest Research Reactor
CERTA	Centre for Emergency Response, Training and Analysis
CFD	computational fluid dynamics
CHF	critical heat flux
CMC	carboxymethyl-cellulose
CNESTEN	Centre National de Énergie, des Sciences et des Techniques Nucléaires, Marokkó
CoCoRAD –	Combined TriTel/Pille Cosmic RADIation and dosimetric measurements
CP-ECR	Cathcart-Pawel Equivalent Cladding Reacted
CCS	carbon capture and storage
CSTP	Council for Science and Technology Policy
DBA	Design Basis Accident
DIM	Dust Impact Monitor
DLR	National Aeronautics and Space Research Centre of Germany
DNBR	Departure from Nucleate Boiling Ratio
DNR	Dinamic radiography
DÖME	Damn heavy measuring equipment
DPU	Digital Processing Unit
EC	European Commission
ECR	Equivalent Cladding Reacted
EIA	environmental impact assessment
EPR	European pressurized water reactor
ESA	European Space Agency
EU	European Union
EVA	Extra-vehicular Activity
FGR	Fission Gas Release
FP	Framework Programmes
FRM-II	Forschungs-Neutronenquelle Heinz Maier-Leibnitz, Technische Universität München (TUM) in Garching
FSAR	Final Safety Analysis Report
FSS	First Scientific Sequence
FTIR	Fourier transform infrared spectroscopy
GFR	gas-cooled fast reactor
GIF	The Generation IV International Forum
GRM	Ground Reference Model
GSE	Ground Support Equipment
HAEA	Hungarian Atomic Energy Authority
HBS	High-Burnup Structure
HEU	Highly enriched uranium

HPLC	High Performance Liquid Chromatography
IBMP	Institute for Biomedical Problems
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
ISS	International Space Station
JSPS	Japan Society for the Promotion of Science
LB	Large Break
LBLOCA	large break LOCA
LeGe	Low-energy germanium detector
LET	Linear Energy Transfer
LEU	Low Enriched Uranium
LOCA	Loss-of-Coolant Accident
LOWG	Lander Operation Working Group
LTS	Long Term Science
MCP	Main Coolant Pump
MFGI	Geological and Geophysical Institute of Hungary
MORABA	Mobile Rocket Base
MPS	Max Planck Institute für Sonnensystemforschung (for Solar System Research)
MS	Mass spectrometry
MSIV	Main Steam Isolation Valve
MTA EK	Hungarian Academy of Sciences Centre for Energy Research
MTC	Moderator Temperature Coefficient of reactivity
MOX	Mixed Oxide
MPI	Message Passage Interface
NAA	Instrumental Neutron Activation Analysis
NCP	Network Control Program
NIPS	Neutron Induced Prompt-gamma spectrometry
NMS	New Member State
NORMA	Neutron Tomography
NPP	Nuclear Power Plant
NT	Neutron Tomography
OCA	Orbiter Communications Adapter
OMS	Old Member State
PAZAR	Hungarian acronym of the Paks Autonomous Noise Data Acquisition System
PAZAR-K	Evaluation system for the data measured by PAZAR
PCI	Pellet Cladding Interaction.
PCI-SCC	Pellet Cladding Interaction - fission products assisted Stress Corrosion Cracking.
PCMI	Pellet Cladding Mechanical Interaction.
PDCS	Pre-Delivery Calibration and Science
PDP	Passive Detector Package
PECS	Plan for European Cooperating States
PGAA	Prompt-Gamma Activation Analysis
PGAI	Prompt Gamma Activation Imaging
PHC	Post Hibernation Commissioning
PRISE	primary to secondary leakage
PSA	Probabilistic Safety Analysis
PWR	Pressurized Water Reactor
R&D	Research and Development
REM-RED	GM Sounding Rocket Experiment to Measure the Cosmic Radiation and Estimate its Dose Contribution
REXUS	Rocket Experiment for University Students
RIA	Reactivity Initiated Accident
ROMAP	Rosetta Lander Magnetometer and Plasma Monitor
SAA	South Atlantic Anomaly
SCWR	Super Critical Water-cooled Reactor
SCWR-FQT	Supercritical Water Reactor-Fuel Qualification Test

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SDL	Separation, Descent and Landing
SEI	Software Engineering Institute
SEM	scanning electron microscopy
SEM-EDX	Scanning electron microscope - Energy dispersive X-ray analysis
SESAME	Surface Electrical, Seismic and Acoustic Monitoring Experiments
SIP	Small Instrument Package
SNSB	Swedish National Space Board
SPM	Simple Plasma Monitor
SRL	Space Robotics Laboratory
SSA	specific surface area
SSC	Swedish Space Corporation
SSNTD	Solid state nuclear track detectors
SURE	International Space Station: a Unique Research Infrastructure
SW	Software
TANDEM	Trans-uranium Actinide Nuclear Data – Evaluation and Measurement
TECHDOSE	Development of a Complex Balloon Technology Platform for Advanced Cosmic Radiation and Dosimetric Measurements
TEM	Transmission electron microscopy
TL	thermoluminescent
TLD	thermoluminescent dosimeter
TPR-TG	temperature-programmed reduction – thermogravimetry
VOF	volume of fluid
VVER	well known Russian reactor type, Russian acronym
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence